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NAVY DEPARTMENT
OFFICE OF NAVAL RESEARCH
WASHINGTON, D.C.

EXPLOSIVES RESEARCH

✦ DO NOT T.I.P.

11 December 1952

Report No. 660
(Quarterly)

EXPLOSIVES RESEARCH

Contract N7onr-46208

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1 August through 31 October 1952

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CONTRACT FULFILLMENT STATEMENT

This quarterly summary report is submitted in partial
fulfillment of Contract N7onr-46208.

I.   SUMMARY

   A.   This quarterly report is submitted under Contract N7onr-46208 and covers the period 1 August through 31 October 1952.* The objectives of the contract are threefold:

   1.   Synthesis and physical studies of new high-energy polynitro compounds as potential explosives.

   2.   Desensitization of RDX wi   materials which will not lower its oxygen balance appreciably.

   3.   Development of bomb and shell casings made of an explosive plastic.

   B.   The more important results and conclusions of the work reported are presented below:

   1.   Five new high explosives, all nitramines, have been synthesized by use of the Mannich condensation:

   a.   The condensation of 3,3,3-trinitropropyl amine and trinitroethanol, followed by postnitration, gave N-2,2,2-trinitroethyl-N-3,3,3-trinitropropyl nitramine.

   b.   The condensation of two moles of 3,3,3-trinitropropyl amine with one mole of 2,2-dinitro-1,3-propanediol, followed by postnitration, gave 1,1,1,4,6,6,8,11,11,11-decanitro-4,8-diaza-undecane.

   c.   The condensation of 3,3,3-trinitropropyl amine with 2,2,4,4-tetranitro-1,5-pentanediol gave N-3,3,3-trinitropropyl-3,3,5,5-tetranitropiperidine.

   d.   The condensation of 3,3,3-trinitropropyl amine with 2,2-dinitropropanol, followed by postnitration, gave N-3,3,3-trinitropropyl-N-2,2-dinitropropyl nitramine.

   e.   The condensation of 3,3-dinitrobutyl amine with trinitroethanol, followed by postnitration, gave N-3,3-dinitrobutyl-N-2,2,2-trinitroethyl nitramine.

   f.   Samples of N-2,2,2-trinitroethyl-N-3,3,3-trinitropropyl nitramine, N-3,3,3-trinitropropyl-N-2,2-dinitropropyl nitramine, and N-3,3-dinitrobutyl-N-2,2,2-trinitroethyl nitramine have been submitted to the Naval Ordnance Laboratory for evaluation.

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*See also Aerojet Reports No. 512 (14 June 1951); No. 538 (11 September 1951); No. 562 (14 December 1951); No. 589 (13 March 1952); No. 621 (6 June 1952); No. 637 (17 September 1952).

2.   The use of the heat of explosion per unit weight is proposed as a criterion of explosive power to supplement the predicted lead-block and ballistic-mortar values. This criterion has the advantage of being the quotient of two terms, each of which (within certain ranges of oxygen balance) has a constant value for any structural alteration, independent of the unaltered portion of the molecule. The contribution to the molar heat of explosion and molecular weight have been tabulated for a large number of structural groups.

3.   The heat of explosion per unit volume has been calculated for a large number of high explosives. The change in the heat of explosion per unit volume for some structural changes has also been calculated.

4.   A method of predicting the crystal density of explosive compounds is under development, and is based on:

       a.   The addition of increments of liquid molecular volume for structural components

       b.   A general relation between calculated liquid densities and experimental crystal densities.

A trial of the method with many explosive compounds shows good agreement of actual and predicted values in most cases, although a few disagreements remain unexplained.

5.   RDX has been desensitized with a 10% coating of a co-polymer of 2,2-dinitrobutyl acrylate (90%) and 2-nitrobutyl acrylate (10%). The 25-g samples with an impact stability of 45 to 50 cm/2 kg on 5/0 sandpaper (Composition A = 55 cm/2 kg) have been submitted to the Naval Ordnance Laboratory for evaluation.

II.   TECHNICAL PROGRESS: SYNTHESIS OF NEW HIGH EXPLOSIVES

      A.   INTRODUCTION

      1.   The present explosives program is directed toward the synthesis of new, stable, high-energy polynitro compounds with a preferred oxygen balance on the positive side or very near zero on the negative side.

      2.   This report deals mainly with the synthesis of nitramines, prepared by means of the Mannich reaction.

      B.   PREPARATION OF 3,3,3-TRINITROPROPYL AMINE HYDROCHLORIDE

      1.   Discussion

      3,3,3-Trinitropropyl amine hydrochloride is a valuable compound in the explosives program, since it might be used as an intermediate

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for the preparation of 3,3,3-trinitropropyl nitramine and Mannich-type condensation products. This compound was synthesized by refluxing a chloroform solution of 3,3,3-trinitropropyl isocyanate with concentrated hydrochloric acid. The hydrochloride salt, obtained in 87% yield, is a non-hygroscopic white crystalline solid (mp = 161 to 163°C dec., I.S. = 40 cm/2 kg).

2.   Experimental

A mixture of 29.7 g (0.126 mole) of 3,3,3-trinitropropyl isocyanate, 50 ml of dry chloroform, and 120 ml of concentrated hydrochloric acid was refluxed for 3 hr and evaporated to dryness in vacuo. The white solid was collected, washed with methylene chloride, and dried in vacuo over potassium hydroxide. The yield of 3,3,3-trinitropropyl amine hydrochloride was 25.5 g (87.7%), (mp 161 to 163°C dec., I.S. = 40 cm/2 kg). A sample was recrystallized three times from nitromethane - ethylene dichloride.

Anal. Calc'd for $C_3H_7N_4O_6Cl$: %C, 15.63; %H, 3.06; %N, 24.40; %Cl, 15.38

Found: %C, 16.04; %H, 3.05; %N, 24.34; %Cl, 15.57

C.   PREPARATION OF N-2,2,2-TRINITROETHYL N-3,3,3-TRINITROPROPYL NITRAMINE

1.   Discussion

a.   The study of the preparation of nitramines as potential high explosives has been continued. One of the most powerful high explosives prepared to date is HOX, or bis(trinitroethyl) nitramine (I). The main disadvantages of HOX are its poor thermal stability at high temperatures and low impact stability. It was therefore of interest to prepare some simple carbon analogs of HOX, such as N-2,2,2-trinitroethyl-N-3,3,3-trinitropropyl nitramine (II) and bis(trinitropropyl) nitramine (III):

$$\underset{\text{(I)}}{\overset{\displaystyle\overset{NO_2}{|}}{N}\left[CH_2C(NO_2)_3\right]_2} \qquad \underset{\text{(II)}}{\overset{\displaystyle\overset{NO_2}{|}}{(NO_2)_3CCH_2CH_2NCH_2C(NO_2)_3}} \qquad \underset{\text{(III)}}{\overset{\displaystyle\overset{NO_2}{|}}{N}\left[CH_2CH_2C(NO_2)_3\right]_2}$$
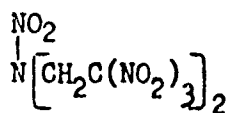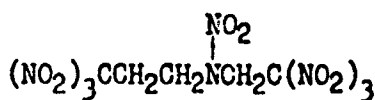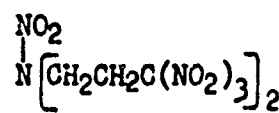
Although compounds (II) and (III) would not possess as favorable an oxygen balance as (I), it was expected that their melting points would be higher (thus probably giving better thermal stability at higher temperatures), and their impact stabilities should be improved.

b.   The method of synthesis of N-2,2,2-trinitroethyl-N-3,3,3-trinitropropyl nitramine (II) is illustrated in the following equations:

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$$(NO_2)_3 CCH_2CH_2NH_2 \cdot HCl + HOCH_2C(NO_2)_3 + NaOH$$

$$\downarrow$$

$$(NO_2)_3 CCH_2CH_2\overset{H}{N}CH_2C(NO_2)_3$$

$$\downarrow \begin{array}{c} HNO_3 \\ Ac_2O \end{array}$$

$$(NO_2)_3 CCH_2CH_2\overset{NO_2}{N}CH_2C(NO_2)_3$$

$$(II)$$
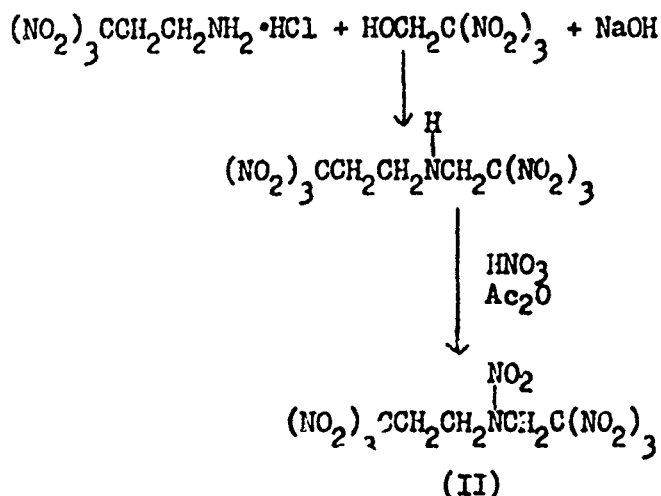
c.   The Mannich condensation of 3,3,3-trinitropropyl amine hydrochloride and trinitroethanol was easily carried out by adding dropwise the stoichiometric amount of sodium hydroxide solution to an aqueous solution of the reactants. The product immediately separated as a yellow oil which crystallized when the reaction mixture was cooled. The yield of N-2,2,2-trinitroethyl-N-3,3,3-trinitropropyl amine was 79% (mp 64 to 65°C, I.S. = 15 cm/2 kg).

d.   N-2,2,2-Trinitroethyl-N-3,3,3-trinitropropyl nitramine (II) was prepared from the corresponding amine by nitration with a mixture of 100% nitric acid and acetic anhydride at 30°C. This new nitramine is a white crystalline solid (mp 144 to 145°C, I.S. = 1 cm/2 kg). As expected, the melting point is higher than that of HOX (mp = 96°C) but, surprisingly, it is much more sensitive to impact than HOX. Compound (II) has a positive oxygen balance of +4; when adjusted to zero oxygen balance with 5% TNT, the calculated lead-block value is 194 (RDX = 157), and the calculated ballistic-mortar value is 154 (RDX = 150).

2.   Experimental

a.   Preparation of N-2,2,2-Trinitroethyl-N-3,3,3-trinitropropyl Amine

An 88-ml quantity of 1.136N sodium hydroxide solution (0.1 mole) was added dropwise at room temperature to a stirred solution of 23.1 g (0.1 mole) of 3,3,3-trinitropropyl amine hydrochloride, 18.1 g (0.1 mole) of trinitroethanol, and 150 ml of water. A yellow oil immediately separated, and on cooling in an ice-bath the oil solidified to a yellow solid. The product was collected, washed with water, and dried. The yield of N-2,2,2-trinitroethyl-N-3,3,3-trinitropropyl amine was 28.2 g (79%), (mp 62 to 65°C, I.S. = 15 cm/2 kg). Recrystallization from chloroform gave yellow needles (mp 64 to 65°C).

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Anal. Calc'd for $C_5H_7N_7O_{12}$: %C, 16.81; %H, 1.98; %N, 27.45

Found: %C, 17.49; %H, 2.11; %N, 27.55

b.   Preparation of N-2,2,2-Trinitroethyl-N-3,3,3-trinitropropyl Nitramine

A 150-ml quantity of 100% commercial nitric acid was placed in a 500-ml three-necked flask, fitted with a mechanical stirrer, thermometer, and dropping funnel. The flask was cooled in an ice-bath and 150 ml of acetic anhydride was added dropwise, keeping the temperature below 10°C. N-2,2,2-Trinitroethyl-N-3,3,3-trinitropropyl amine (28.2 g) was added to the mixed acid. Solution did not occur until the temperature was raised to 30°C. The solution was filtered free of a small amount of solid and poured onto ice. The white solid was collected, washed with water, and dried in vacuo over potassium hydroxide to give 27 g of the nitramine (mp 115 to 122°C). Four recrystallizations from chloroform gave white needles (mp 144 to 145°C, I.S. = 1 cm/2 kg).

Anal. Calc'd for $C_5H_6N_8O_{14}$: %C, 14.93; %H, 1.50; %N, 27.86

Found: %C, 15.23; %H, 1.60; %N, 28.13

Heat of Combustion, ΔH_p, Predicted: 1611 cal/g

Found: 1609 cal/g

D.   PREPARATION OF 1,1,1,4,6,6,8,11,11,11-DECANITRO-4,8-DIAZA-UNDECANE

1.   Discussion

Upon continuation of the study of the Mannich condensations of 3,3,3-trinitropropyl amine, it has been found that two moles of the amine will condense with one mole of 2,2-dinitro-1,3-propanediol to form 1,1,1,6,6,11,11,11-octanitro-4,8-diaza-undecane (IV). Nitration of (IV) with a mixture of 100% nitric acid and acetic anhydride gave the compound 1,1,1,4,6,6,8,11,11,11-decanitro-4,8-diaza-undecane (V).

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$$2(NO_2)_3CCH_2CH_2NH_2 \cdot HCl \; + \; HOCH_2 \overset{\overset{\displaystyle NO_2}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}} CH_2OH$$

$$\Big\downarrow \; 2 \text{ aOH}$$

$$\overset{\overset{\displaystyle NO_2}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}} \Big[CH_2 \overset{\overset{\displaystyle H}{|}}{N} CH_2CH_2C(NO_2)_3 \Big]_2$$

(IV)

$$\Big\downarrow \; \begin{array}{l} HNO_3 \\ Ac_2O \end{array}$$

$$\overset{\overset{\displaystyle NO_2}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}} \Big[CH_2 \overset{\overset{\displaystyle NO_2}{|}}{N} CH_2CH_2C(NO_2)_3 \Big]_2$$

(V)
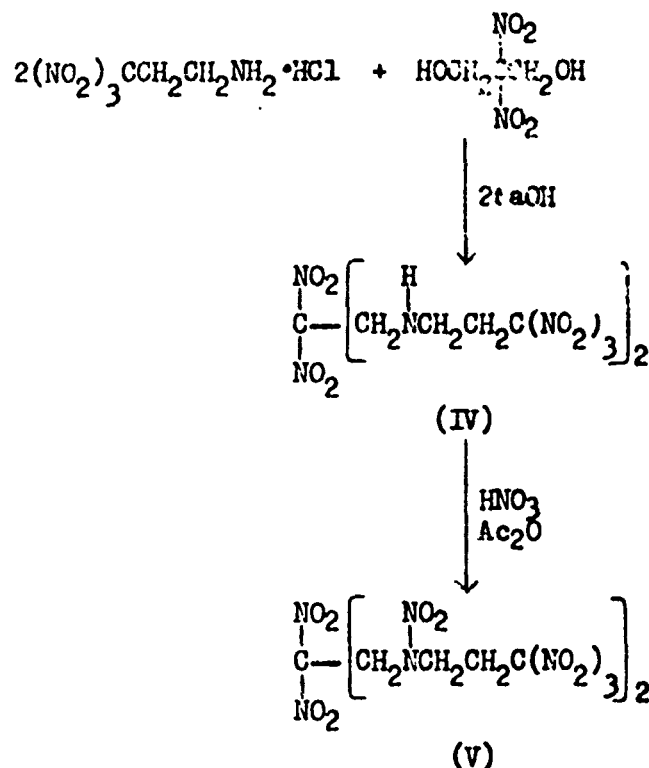
(V) is a white crystalline compound (mp 135 to 137°C dec., I.S. = 10-15 cm/2 kg) with a calculated lead-block value of 177 and a calculated ballistic-mortar value of 155.

2.   Experimental

a.   Preparation of 1,1,1,6,6,11,11,11-Octanitro-4,8-diaza-undecane

A solution of 8.3 g (0.05 mole) of 2,2-dinitro-1,3-propanediol, 23.0 g (0.10 mole) of 3,3,3-trinitropropyl amine hydrochloride, and 50 ml of water was placed in a 300-ml three-necked flask, fitted with a mechanical stirrer. A solution of 88 ml of 1.136N sodium hydroxide (0.10 mole) was added dropwise from a burette. The addition of the base caused a yellow solid to precipitate. The product was collected, washed with water, and dried to give 21.7 g (83.8%) of tan solid (mp 70 to 80°C dec.).

b.   Preparation of 1,1,1,4,6,6,8,11,11,11-Decanitro-4,8-diaza-undecane

A solution of 40 ml of 100% nitric acid and 40 ml of acetic anhydride was cooled to 5°C, and 4.1 g of 1,1,1,6,6,11,11,11-octanitro-4,8-diaza-undecane was added. On warming to room temperature the

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solid dissolved. The solution was poured on ice, causing a cream-colored, gummy solid to precipitate. The product was collected, washed with water, and dried, to yield 2.4 g. Several recrystallizations from concentrated nitric acid gave white needles (mp 135 to 137°C dec., I.S. = 10 to 15 cm/2 kg).

Anal. Calc'd for $C_9H_{12}N_{12}O_{20}$: %C, 17.77; %H, 1.99; %N, 27.64

Found: %C, 18.39; %H, 1.99; %N, 28.24

E.   PREPARATION OF N-3,3,3-TRINITROPROPYL-3,3,5,5-TETRANITROPIPERIDINE

1.   Discussion

a.   The preparation of 3,3,5,5-tetranitropiperidine (VI) by the Mannich condensation of 2,2,4,4-tetranitro-1,5-pentanediol and ammonium acetate, and the conversion of (VI) to N-2,2,2-trinitroethyl-3,3,5,5-tetranitropiperidine (VII) has been reported previously.*
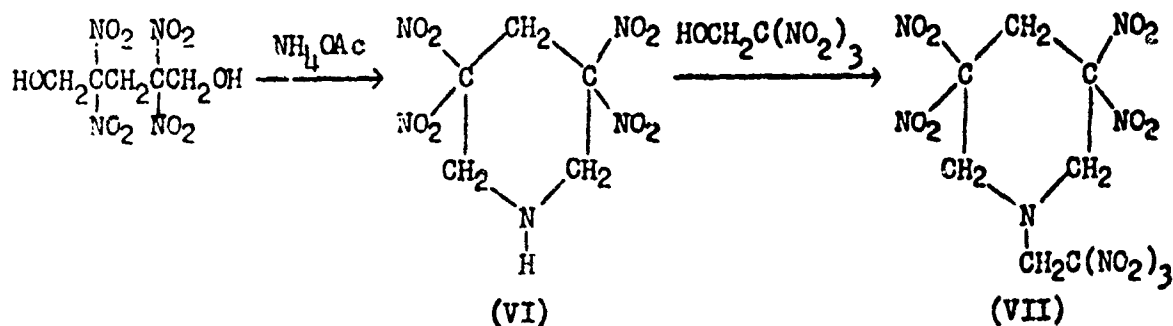
b.   It has now been found that a similar condensation occurs between 2,2,4,4-tetranitro-1,5-pentanediol and 3,3,3-trinitropropyl amine, with the formation of N-3,3,3-trinitropropyl-3,3,5,5-tetranitropiperidine (VIII):
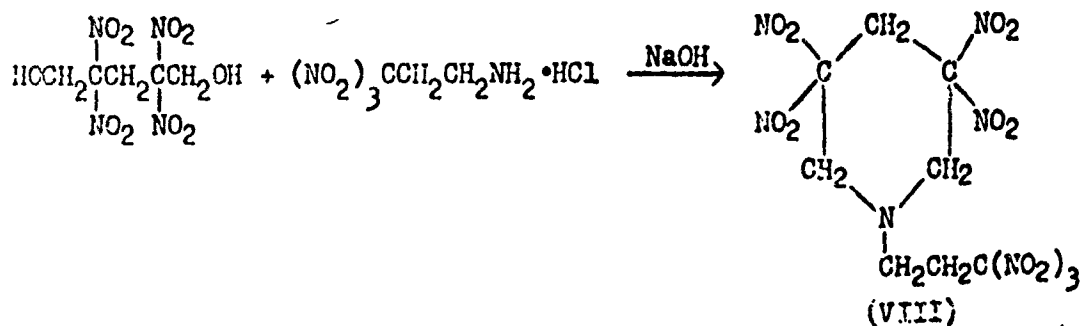
A comparison of the properties of (VII) and (VIII) is shown below:

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*Aerojet Report No. 637, p. 2.

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	mp, °C dec.	I.S. cm/2 kg	Calculated Lead-Block Value	Calculated Ballistic-Mortar Value
N-2,2,2-Trinitroethyl-3,3,5,5-tetranitro-piperidine	163 to 168	20	170	153
N-3,3,3-Trinitropropyl-3,3,5,5-tetranitro-piperidine	142 to 144	25	154.5	151.5

2. Experimental

A mixture of 4.6 g (0.02 mole) of 3,3,3-trinitropropyl amine hydrochloride, 5.68 g (0.02 mole) of 2,2,4,4-tetranitro-1,5-pentanediol, and 60 ml of water was warmed to 35°C to effect solution. A solution of 176 ml of 1.136N sodium hydroxide (0.02 mole) was added from a burette, causing a cream-colored solid to precipitate. The mixture was stirred for 30 min and cooled to 5°C. The solid was collected, washed with water, and dried; the yield was 3.3 g (mp 89 to 93°C dec.). Three recrystallizations from concentrated nitric acid gave white plates (mp 142 to 144°C dec., I.S. = 25 cm/2 kg).

Anal. Calc'd for $C_8H_{10}N_8O_{14}$: %C, 21.73; %H, 2.28; %N, 25.34

Found: %C, 21.33; %H, 2.29; %N, .52

F. THE INFLUENCE OF THE N-NITRO-N-TRINITROETHYL GROUPING ON THE STABILITY OF HIGH EXPLOSIVES

1. The Naval Ordnance Laboratory has reported that all of the seven high explosives containing the structure $(NO_2)_3CCH_2N$ tended to be
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | $
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad NO_2$

very sensitive to impact and to possess poor thermal stability.[*] Inasmuch as secondary nitramines are generally quite stable thermally, the NOL workers postulated that the instability of these seven compounds may be due to a combination of the close proximity of the powerfully negative trinitromethyl group to the nitramine group with a corresponding weakening of the bond in the latter, together with the steric strain in the molecule.

2. In order to test the validity of this correlation between chemical structure and stability and to try to determine whether the N-nitro-N-trinitroethyl grouping is practical for a Service explosive, the present work was aimed at synthesizing two isomeric compounds, only one of which would contain the N-nitro-N-trinitroethyl grouping. For this purpose N-3,3,3-trinitropropyl-N-2,2-dinitropropyl nitramine (IX) and N-3,3-dinitrobutyl-N-2,2,2-trinitroethyl nitramine (X) have been prepared (see II, G and II, H):

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[*]NavORD Report 2448, 6 June 1952.

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$$(NO_2)_3CCH_2CH_2NCH_2CCH_3 \qquad CH_3CCH_2CH_2NCH_2C(NO_2)_3$$
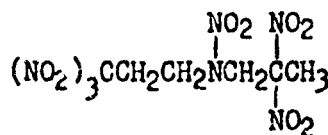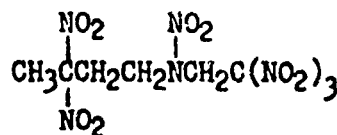
(IX)   (X)

These compounds have been submitted to the Naval Ordnance Laboratory for evaluation. The result of this study may throw some light on the relation of chemical structure to stability.

G.   PREPARATION OF N-3,3,3-TRINITROPROPYL-N-2,2-DINITROPROPYL NITRAMINE

1.   Discussion

The condensation of 3,3,3-trinitropropyl amine and 2,2-dinitropropanol gave N-3,3,3-trinitropropyl-N-2,2-dinitropropyl amine (XI), an amber oil. Nitration of this oil with a mixture of 100% nitric acid and acetic anhydride yielded N-3,3,3-trinitropropyl-N-2,2-dinitropropyl nitramine (XII):

$$(NO_2)_3CCH_2CH_2NH_2 \cdot HCl + HOCH_2CCH_3 \xrightarrow{NaOH} (NO_2)_3CCH_2CH_2NCH_2CCH_3$$
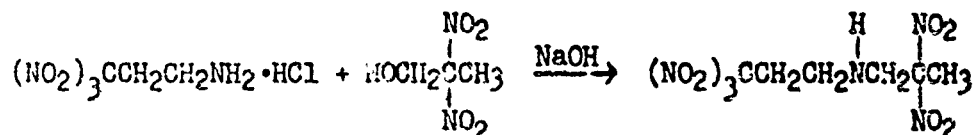
(XI)

$$\Bigg\downarrow \begin{array}{c} HNO_3 \\ Ac_2O \end{array}$$

$$(NO_2)_3CCH_2CH_2NCH_2CCH_3$$
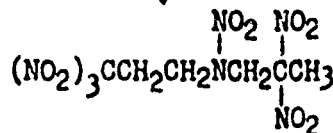
(XII)

(XII) is a cream-colored solid (mp 109 to 109.5°C dec., I.S. = 35 to 40 cm/2 kg) with a calculated lead-block value of 162, and a calculated ballistic-mortar value of 153.

2.   Experimental

A 17.6-ml quantity of 1.136N sodium hydroxide solution (0.02 mole) was added from a burette to a solution of 4.6 g (0.02 mole) of

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II Technical Progress, G (cont.)   Report No. 660

3,3,3-trinitropropyl amine hydrochloride, 3.3 g (0.022 mole) of 2,2-dinitro-propanol, and 40 ml of water. The yellow oil was extracted with methylene chloride, dried, and concentrated to give 7.3 g of amber liquid. The liquid was taken up in 50 ml of acetic anhydride, and the solution was added dropwise to 50 ml of 100% nitric acid at 5°C. The acid solution was poured on ice, precipitating a cream-colored solid which was collected, washed with water, and dried. The weight was 5.1 g, and the mp was 93 to 103°C dec. A sample was recrystallized three times from carbon tetrachloride to give cream-colored plates (mp 109 to 109.5°C dec., I.S. = 35 to 40 cm/2 kg).

Anal. Calc'd for $C_6H_9N_7O_{12}$: %C, 19.41; %H, 2.44; %N, 26.42

Found: %C, 19.90; %H, 2.52; %N, 26.91

Heat of Combustion, ΔH_p, Predicted: 2232 cal/g

Found: 2298 cal/g

H.   PREPARATION OF N-3,3-DINITROBUTYL-N-2,2,2-TRINITROETHYL NITRAMINE

   1.   Discussion

The condensation of 3,3-dinitrobutyl amine[*] and trinitro-ethanol gave N-3,3-dinitrobutyl-N-2,2,2-trinitroethyl amine (XIII), a yellow oil. Nitration of this oil with a mixture of 100% nitric acid and acetic anhydride yielded N-3,3-dinitrobutyl-N-2,2,2-trinitroethyl nitramine (XIV).

$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2NH_2 \cdot HCl + HOCH_2C(NO_2)_3 \xrightarrow{NaOH} CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\overset{H}{N}CH_2C(NO_2)_3$$

(XIII)

$$\downarrow \begin{matrix} HNO_3 \\ Ac_2O \end{matrix}$$

$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\overset{NO_2}{N}CH_2C(NO_2)_3$$

(XIV)
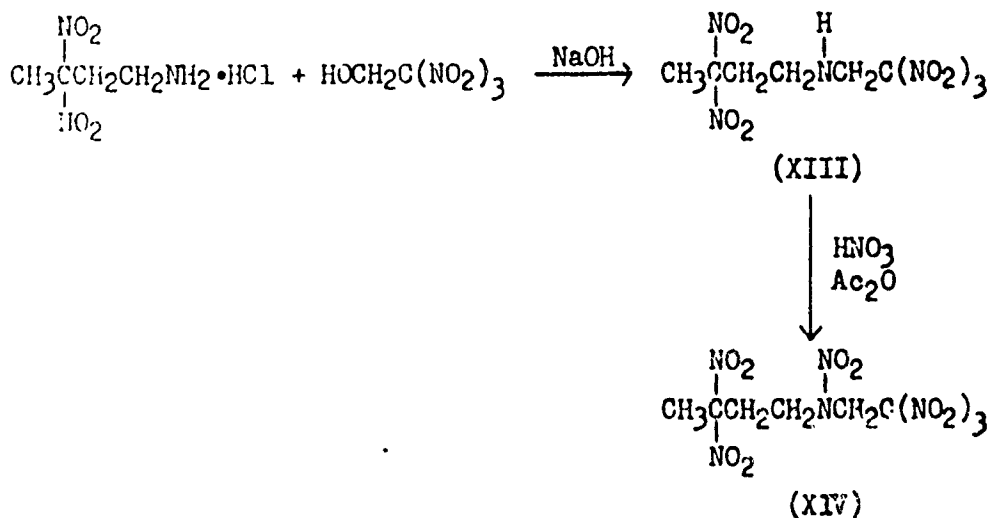
(XIV) is a cream-colored solid (mp 105 to 107°C dec., I.S. = 25 cm/2 kg) with a calculated lead-block value of 162, and a calculated ballistic-mortar value of 133.

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[*] Aerojet Report No. 638, p. 101.

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2. Experimental

A 132-ml quantity of 1.136N sodium hydroxide solution (0.15 mole) was added from a burette to a solution of 30.0 g (0.15 mole) of 3,3-dinitrobutyl amine hydrochloride, 27 g (0.15 mole) of trinitroethanol, and 100 ml of water. The oil was extracted with methylene chloride, dried, and concentrated to give 38.5 g of amber liquid. The liquid was dissolved in 200 ml of acetic anhydride and the solution was added dropwise to 200 ml of 100% nitric acid at $5^{\circ}C$. The solution was then poured on ice, giving a yellow oil which crystallized slowly. The solid was collected, washed with water, dried, and recrystallized from chloroform to give 16.6 g of cream-colored solid (mp 80 to $95^{\circ}C$ dec.). A sample was recrystallized four times from chloroform to give cream-colored needles (mp 105 to $107^{\circ}C$ dec., I.S. = 25 cm/2 kg).

Anal. Calc'd for $C_6H_9N_7C_{12}$: %C, 19.44; %H, 2.44; %N, 26.42

Found: %C, 20.18; %H, 2.53; %N, 26.44

Heat of Combustion, ΔH_p, Predicted: 2232 cal/g

Found: 2229 cal/g

I. ATTEMPTED CONDENSATION OF 3,3,3-TRINITROPROPYL AMINE HYDROCHLORIDE WITH ETHYL OXALATE AND POTASSIUM CYANATE

1. Discussion

The successful condensation of 3,3,3-trinitropropyl amine hydrochloride with the foregoing nitroalcohols prompted an investigation into other condensation reactions in which this amine might be utilized. Consequently, the condensation of 3,3,3-trinitropropyl amine hydrochloride with ethyl oxalate and potassium cyanate was studied with the expectation of forming substituted amides which might have value as potential explosives after postnitration:

$$(NO_2)_3CCH_2CH_2NH_2 \cdot HCl + (CO_2Et)_2 \longrightarrow \left[\begin{matrix} O\ H \\ \| \ / \\ CNCH_2CH_2C(NO_2)_3 \end{matrix} \right]_2$$

$$(NO_2)_3CCH_2CH_2NH_2 \cdot HCl + KOCN \longrightarrow (NO_2)_3CCH_2CH_2NCNH_2$$
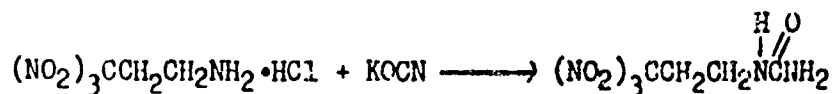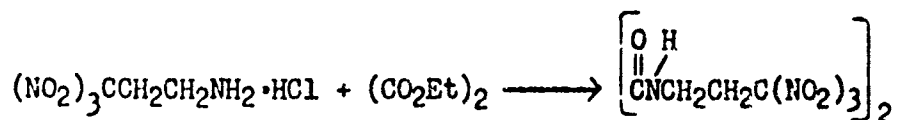
The first condensation gave a yellow-red solid and the second a yellow oil. Nitration of these products yielded water-soluble materials.

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II Technical Progress, I (cont.)   Report No. 66C

2. Experimental

a. Condensation of 3,3,3-Trinitropropyl Amine Hydrochloride and Ethyl Oxalate

A 17.60-ml quantity of 1.136N sodium hydroxide solution (0.02 mole) was added dropwise at room temperature to a solution of 4.6 g (0.02 mole) of 3,3,3-trinitropropyl amine hydrochloride in 15 ml of water and 1.46 g (0.01 mole) of ethyl oxalate in 10 ml of methanol. After a short time a yellow-red oil separated which solidified on cooling. The solid was collected, dried, and added to 50 ml of an equal mixture of 100% nitric acid and acetic anhydride. When this solution was poured on ice, there was no precipitation of solid.

b. Condensation of 3,3,3-Trinitropropyl Amine Hydrochloride and Potassium Cyanate

When 2.3 g (0.01 mole) of 3,3,3-trinitropropyl amine hydrochloride was mixed with 0.83 g (0.01 mole) of 97.6% potassium cyanate and 10 ml of water, a yellow oil was precipitated. Addition of this oil to a nitrating mixture of 100% nitric acid and acetic anhydride gave water-soluble products.

J. ATTEMPTED PREPARATION OF NITRAMIDES BY THE ADDITION OF ACIDS TO ISOCYANATES

1. Introduction

Aliphatic isocyanates react with organic acids to form acid anhydrides, which lose carbon dioxide to yield substituted amides:[*]

$$RNCO + R'CO_2H \longrightarrow \underset{RNC-CCR'}{\overset{H\ O\ \ O}{}} \longrightarrow \underset{RNC-R'}{\overset{H\ O}{}} + CO_2$$
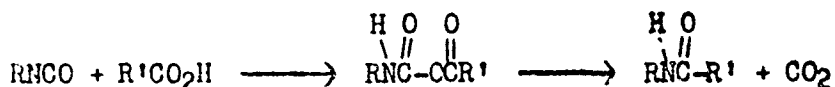
It was of interest to determine whether this reaction could be applied to the preparation of substituted amides wherein R and R' contained polynitro groups. Nitration of these substituted amides would give nitramides of high explosive power. The addition of 4,4,4-trinitrobutyric acid and N-trinitro-ethyl-N-nitroglycine to 3,3,3-trinitropropyl isocyanate was studied with the expectation of preparing the following compounds:

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[*]Naegeli and Tyabji, Helv. Chim. Acta 17, 947 (1934).

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II Technical Progress, J (cont.)   Report No. 660

$$(NO_2)_3CCH_2CH_2NCO + (NO_2)_3CCH_2CH_2CO_2H \longrightarrow$$

$$(NO_2)_3CCH_2CH_2\overset{\overset{H}{\underset{|}{N}}\overset{O}{\overset{||}{C}}}{N}CCH_2CH_2C(NO_2)_3 + CO_2$$

$$(NO_2)_3CCH_2CH_2NCO + (NO_2)_3CCH_2\overset{\overset{NO_2}{|}}{N}CH_2CO_2H \longrightarrow$$

$$(NO_2)_3CCH_2CH_2\overset{\overset{H}{\underset{|}{N}}\overset{O}{\overset{||}{C}}}{N}CCH_2\overset{\overset{NO_2}{|}}{N}CH_2C(NO_2)_3 + CO_2$$
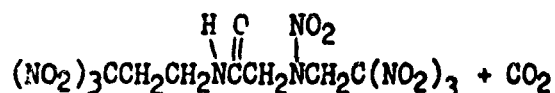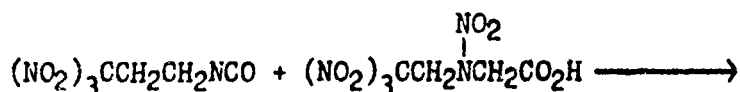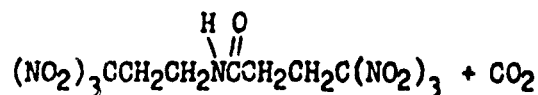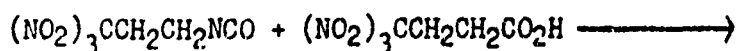
2. Discussion

a. When a chloroform solution of 3,3,3-trinitropropyl isocyanate and 4,4,4-trinitrobutyric acid was warmed, a vigorous evolution of gas occurred and a white solid precipitated. However, this product was not the expected amide but rather bis(trinitropropyl) urea. Naegeli reported that the main product from the reaction of aromatic isocyanates and organic acids was disubstituted ureas.[*]

b. There was little evidence of reaction between 3,3,3-trinitropropyl isocyanate and N-trinitroethyl N-nitroglycine.

3. Experimental

a. A solution of 6.6 g (0.03 mole) of 3,3,3-trinitropropyl isocyanate, 6.6 g (0.03 mole) of 4,4,4-trinitrobutyric acid and 50 ml of dry chloroform was warmed to reflux temperature. Gas evolution commenced, and after 15 min a white solid separated. Refluxing was continued for 2 hr, and the solid was then collected and dried; the weight of crude product was 8.1 g. A sample was recrystallized three times from ethylene dichloride to give long white needles (mp 162 to 164°C dec., I.S. = 25 cm/2 kg).

Anal. Calc'd for $C_7H_{10}N_8O_{13}$:   %C, 20.30; %H, 2.43; %N, 27.05

Found: %C, 20.97; %H, 2.62; %N, 28.47

b. A solution of 6.6 g (0.03 mole) of 3,3,3-trinitropropyl isocyanate, 8.5 g (0.03 mole) of N-trinitroethyl N-nitroglycine, and 100 ml of dry chloroform was refluxed for 22 hr. The yellow solution was filtered free of 5.9 g of unreacted acid and evaporated, leaving 6.2 g of an orange oil which could not be crystallized.

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[*]Loc. cit.

K. ATTEMPTED PREPARATION OF N-TRINITROETHYL UREA

1. Discussion

In continuation of the work on the preparation of nitramides, work was initiated on the synthesis of N-nitro-N'-trinitroethyl urea. The method of approach was the following:

$$NH_2\overset{\overset{O}{\|}}{C}\text{-}NH_2 \xrightarrow{CH_2O} NH_2\overset{\overset{O}{\|}}{C}NHCH_2OH \xrightarrow{HC(NO_2)_3}$$

$$NH_2\overset{\overset{O}{\|}}{C}\text{-}NHCCH_2C(NO_2)_3 \xrightarrow{HNO_3} NO_2\overset{\overset{H}{\diagdown}\overset{OH}{\diagup}}{N}\overset{}{C}NCH_2C(NO_2)_3$$
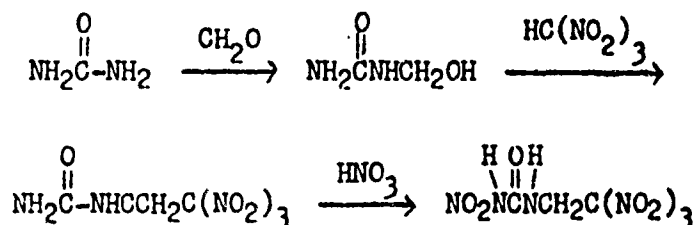
The addition of nitroform to an aqueous solution of N-methylol urea caused a solid to precipitate. However, the analysis of this product did not correspond to that of the expected N-trinitroethyl urea, indicating that this is not a straightforward reaction. Therefore it will not be investigated further.

2. Experimental

a. In a 150-ml beaker was placed 30 g (0.5 mole) of urea and 10 ml of water (pH = 8.1). A quantity of 40.6 g (0.5 mole) of 37% formaldehyde was added dropwise, and a small amount of barium hydroxide was added during the addition to maintain the pH at 7 to 8. After the addition, carbon dioxide was added to precipitate the barium hydroxide, and the pH dropped to 6. The reaction mixture was filtered and evaporated to dryness in a desiccator. The white solid obtained was recrystallized from ethanol, and the yield of N-methylol urea was 26.0 g (57.8%), mp ca 80°C.

b. When 15.1 g (0.1 mole) of nitroform, 9.0 g (0.1 mole) of N-methylol urea, and 50 ml of water were mixed, there was an immediate precipitation of a yellow solid. The reaction mixture was warmed to 60°C, cooled, and filtered. The product was washed with water and dried to give 9.7 g of white solid. A sample was recrystallized three times from acetone-water; the mp was ca 230°C.

Anal. Calc'd for $C_3H_5N_5O_7$: %C, 16.15; %H, 2.26; %N, 31.39

Found: %C, 19.69; %H, 2.50; %N, 30.00

L. ATTEMPTED PREPARATION OF 2-ACETAMIDO-4,4,4-TRINITROBUTYRIC ACID

1. Discussion

4,4,4-Trinitrobutyric acid, prepared by the addition of nitroform to acrylic acid, has been very useful in the synthesis of high-energy compounds. An analogous compound of even higher energy content is

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II Technical Progress, L (cont.)   Report No. 660

2-nitramino-4,4,4-trinitrobutyric acid, which might be prepared in the following manner:

$$CH_2\text{=}CCO_2H + HC(NO_2)_3 \longrightarrow (NO_2)_3CCH_2CHCO_2H$$
$$\overset{|}{NHCOCH_3} \qquad\qquad\qquad\qquad\quad \overset{|}{NHCOCH_3}$$

$$\longrightarrow (NO_2)_3CCH_2CHCO_2H \longrightarrow (NO_2)_3CCH_2CHCO_2H$$
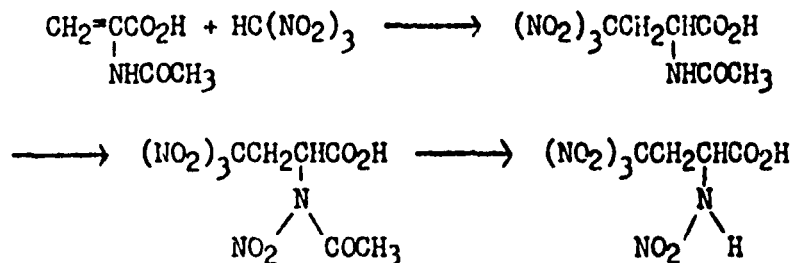
However, the nitroform addition to 2-acetamido acrylic acid did not take place.

2. Experimental

In a 100-ml 3-necked flask, fitted with a mechanical stirrer, thermometer, and dropping funnel, was placed 2.58 g (0.02 mole) of 2-acetamido acrylic acid and 75 ml of methanol. A solution of 3.02 g (0.02 mole) of nitroform in 10 ml of water was added. On warming to 40°C, a clear yellow solution was obtained. The solution was stirred for 2 hr and evaporated to dryness, leaving 1.5 g of 2-acetamido acrylic acid.

M. PREPARATION OF 2-NITROBUTYL ACRYLATE

1. Discussion

2-Nitrobutyl acrylate was desired as a coating agent for RDX. The preparation of this monomer was carried out in two ways:

a. The esterification of 2-nitrobutanol at 40°C with an excess of acrylic acid and sulfuric acid gave a 42% yield of 2-nitrobutyl acrylate.

b. The esterification of 2-nitrobutanol in refluxing benzene with acrylic acid and a catalytic amount of sulfuric acid gave 2-nitrobutyl acrylate in yields of 53.4 to 74.5%. One run was made in which the 2-nitrobutanol was water-washed before use, and the yield of ester in this case was 52%.

2. Experimental

a. In a two-liter three-necked flask, fitted with a mechanical stirrer, thermometer, and dropping funnel, was placed 119 g (1 mole) of 2-nitrobutanol and 288 g (4 moles) of glacial acrylic acid

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stabilized with methylene blue. A 344-g quantity (3.37 moles) of concentrated sulfuric acid was added dropwise, keeping the temperature below 40°C. After addition was complete the temperature was maintained at 40°C for 16 hr. The solution was poured onto 1200 g of crushed ice. The layers were separated, and the water layer was washed with two 250-ml portions of benzene. The organic layers were combined, washed with five 250-ml portions of water, three 250-ml portions of 5% sodium bicarbonate, and two 250-ml portions of water. The solution was dried over sodium sulfate, concentrated, and distilled. The yield of 2-nitrobutyl acrylate was 73 g (42%), bp 81 to 88°C (2 mm), n_D^{25} 1.4660. Bulk polymerization of this monomer gave a soft, rubbery polymer, partially soluble in acetone.

b. In a two-liter three-necked flask, fitted with a Dean-Stark water trap and reflux condenser, was placed 119 g (1 mole) of 2-nitrobutanol, 108 g (1.5 moles) of glacial acrylic acid stabilized with methylene blue, 500 ml of benzene, and 2 ml of concentrated sulfuric acid. After 40 hr of refluxing, 22 ml of water was removed. The solution was filtered, diluted with 250 ml of benzene, and washed with five 250-ml portions of water, three 250-ml portions of 5% sodium bicarbonate, and two 250-ml portions of water. The solution was dried over sodium sulfate, concentrated, and distilled. The yield of 2-nitrobutyl acrylate was 129 g (74.5%), bp 77 to 79°C (2 mm), n_D^{25} 1.4460.

Anal. Calc'd for $C_7H_{11}NO_4$: %C, 48.55; %H, 6.40; %N, 8.08

Found: %C, 48.34; %H, 6.50; %N, 7.95

Bulk polymerization of this monomer with 1% methyl amyl ketone peroxide for 48 hr at 45°C gave a soft, rubbery polymer that was insoluble in acetone.

N. PREPARATION OF 2-NITROISOBUTYL ACRYLATE

1. Discussion

a. In connection with the synthesis of nitrobutyl acrylates for use as coating agents for RDX, 2-nitroisobutyl acrylate has now been prepared.

b. The esterification of 2-nitroisobutanol in refluxing benzene with acrylic acid and a catalytic amount of sulfuric acid gave a 59% yield of 2-nitroisobutyl acrylate.

2. Experimental

In a two-liter three-necked flask, fitted with a Dean-Stark water trap and reflux condenser, was placed 119 g (1 mole) of 2-nitroisobutanol, 87 g (1.2 moles) of glacial acrylic acid stabilized with methylene blue, 300 ml

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of benzene, and 2 ml of concentrated sulfuric acid. After 10 hr of refluxing, 21 ml of water was removed. The reaction mixture was diluted with 300 ml of benzene, washed with water, 5% sodium bicarbonate, and water, then dried, concentrated, and distilled. The yield of 2-nitroisobutyl acrylate was 102 g (59%), bp 72°C (1 micron), n_D^{25} 1.4466.

Anal. Calc'd for $C_7H_{11}NO_4$:   %C, 48.55; %H, 6.40; %N, 8.03

Found: %C, 47.98; %H, 6.48; %N, 8.24

O.   PREPARATION OF 2-NITRO-2-ETHYL-1,3-DIACRYLOXYPROPANE

1.   Discussion

2-Nitro-2-ethyl-1,3-diacryloxypropane was desired for copolymerization with 2,2-dinitrobutyl acrylate in the program on the desensitization of RDX. This monomer was synthesized in 56.8% yield by the esterification of 2-nitro-2-ethyl-1,3-propanediol in refluxing benzene with acrylic acid and a catalytic amount of concentrated sulfuric acid.

2.   Experimental

In a two-liter three-necked flask, fitted with a Barrett-type water separator and condenser, was placed 149 g (1 mole) of 2-nitro-2-ethyl-1,3-propanediol, 216 g (3 moles) of glacial acrylic acid (stabilized with methylene blue), 750 ml of benzene, and 2 ml of concentrated sulfuric acid. The solution was refluxed for 30 hr, filtered, washed with five 250-ml portions of water, three 250-ml portions of 5% sodium bicarbonate, and two 250-ml portions of water, then dried over sodium sulfate, concentrated, and distilled. The yield of 2-nitro-2-ethyl-1,3-diacryloxypropane was 146 g (56.8%), bp 135°C (10 microns), n_D^{25} 1.4678.

Anal. Calc'd for $C_{11}H_{15}NO_6$:   %C, 51.36; %H, 5.88; %N, 5.45

Found: %C, 50.93; %H, 5.98; %N, 5.47

P.   PREPARATION OF SAMPLES FOR EVALUATION BY THE NAVAL ORDNANCE LABORATORY

The following samples were prepared and submitted to the Naval Ordnance Laboratory for evaluation:

1.   N-3,3,3-Trinitropropyl-N-2,2,2-trinitroethyl nitramine, 2 g (mp 144 to 145°C, I.S. = 1 cm/2 kg).

2.   N-3,3,3-Trinitropropyl-N-2,2-dinitropropyl nitramine, 2.7 g (mp 109 to 109.5°C dec., I.S. = 35 to 40 cm/2 kg).

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   3.   N-3,3-Dinitrobutyl-N-2,2,2-trinitroethyl nitramine, 3.0 g
(mp 105 to 107°C dec., I.S. - 25 cm/2 kg).

   4.   Two 25-g samples of RDX with a 10% coating of a co-polymer of
2,2-dinitrobutyl acrylate (90%) and 2-nitrobutyl acrylate (10%) (I.S. - 45 to
50 cm/2 kg on 5/0 sandpaper).

III.   HEAT OF EXPLOSION AS A CRITERION OF EXPLOSIVE POWER

A.   DISCUSSION

   1.   A need exists for a method of comparing quickly the explosive
power of structures. In reports of this series, explosive compounds are
rated by predicted lead-block and ballistic-mortar test values. However,
these properties have the disadvantage that each must be calculated separately,
by a rather cumbersome procedure, for all structures under consideration.

   2.   Moreover, neither of these properties, nor any other, is
accepted as a unique measure of explosive power. Thus, for survey work, it
would be convenient to use some additional property providing a quick
visualization of the gain or loss of power resulting from a particular
structural alteration.

   3.   Use of the heat of explosion per unit weight as a supple-
mentary criterion is now proposed. It is a linear function of the predicted
lead-block value.* In addition, it has the advantage of being the quotient
of two terms, each of which (within certain ranges of oxygen balance) has a
constant value for any structural alteration, independent of the unaltered
portion of the molecule. For example, the effect of oxidizing a hydroxyl
group to a carboxyl group can be shown by simple combination of pairs of
values of ΔH_E and ΔM, taken from a table. If ΔH_E is plotted as ordinate
against ΔM as abscissa, a structural change is represented by a line of
constant magnitude and direction, and complicated changes can be represented
by a vectorial addition of several such lines. If H_E/M, the slope of a straight
line passing through the origin, is higher at the final point than at the
initial point, the over-all change has improved the explosive power.

B.   CALCULATION OF HEATS OF EXPLOSION

   1.   Constancy of increments of H_E follows from the expressions

$$H_E = 10\Delta E - 308\ C + 575\ O + 98\ CO_2^{**}$$

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*Aerojet Report No. 512, p. 11.

**Ibid., p. 13.

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III Heat of Explosion as a Criterion of Explosive   Report No. 660
      Power, B (cont.)

and

$$\Delta E = \frac{100}{M} Q_p - 94.0\ C - 33.9\ H + 0.3\ (O + N)^*$$

Following the assumption that decomposition of an explosive compound contain-
ing carbon, hydrogen, nitrogen, and oxygen takes place in such a way as to
oxidize successively all C to CO, all H to H_2O, and then CO to CO_2, there
are three conditions of oxygen balance of interest:

   a. All C $\longrightarrow$ CO, some H $\longrightarrow$ H_2O

   b. All C $\longrightarrow$ CO, all H $\longrightarrow$ H_2O, some CO $\longrightarrow$ CO_2

   c. Excess oxygen present

A particular structural change produces constant values of ΔQ (as predicted
by the Kharasch method), ΔC, ΔH, and ΔN which are independent of the remainder
of the molecule. Changes in O and CO_2 depend on the condition of oxygen
balance which prevails as well as on the nature of the structural change, but
are constant within any condition.

   2. Values of ΔH_E for a number of structural alterations are
given in Table I. These values were calculated from the equation and from the
Kharasch method of predicting Q.** They are tabulated for each of the three
conditions; values for transitions from one condition to another are inter-
mediate. The corresponding figures for ΔM, the change in molecular weight,
are given in an adjoining column, and in some instances, values of the ratio
$\Delta H_E/\Delta M$. For the purposes of comparison with the tabulated values of $\Delta H_E/\Delta M$,
the heats of explosion of good high explosives are recalled to be about 1.2 to
1.6 kcal/g.

   3. The table shows strikingly that substitution of oxygen-rich
groups is most effective within condition b.

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*Aerojet Report No. 538, p. 22.
**Aerojet Reports No. 345, 417A.

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III. Heat of Explosion as a Criterion of Explosive   Report No. 660
    Power, B (cont.)

TABLE I

HEAT OF EXPLOSION ACCOMPANYING STRUCTURAL ALTERATIONS

Alteration	Change in Molar Heat of Explosion, ΔH_E, kcal, Under Following Conditions*			ΔM	Maximum $\Delta H_E/\Delta M$, kcal/g
	a	b	c		
Substitute for H in saturated hydrocarbon structure:					
Primary OH	+18.7	+28.5	-38.8	+16	+1.78
Secondary OH	+12.2	+22.0	-45.3	+16	+1.38
Tertiary OH	+9.2	+19.0	-48.3	+16	+1.19
Aldehyde O(for 2 H's)	+34.4	+54.0	-80.5	+14	+3.86
Carboxylic COOH	-9.2	+0.6	+0.6	+44	
Primary amine NH₂	+5.4	+0.5	+34.2	+15	
Primary amide CONH₂	-22.4	-27.3	+73.7	+43	
Nitrile CN	+4.1	-0.8	+100.2	+25	
Methyl group CH₃	-36.3	-55.9	+146.0	+14	
Phenyl group C₆H₅	-158.5	-236.9	+705.3	+76	
Nitrate ONO₂	+156.5	+190.8	-44.8	+61	+3.12
Nitro NO₂	+110.7	+135.2	-33.1	+45	+3.00
(NO₂)₂ for 2H	+227.4	+276.4	-60.1	+90	+3.07
(NO₂)₃ for 3H	+353.1	+426.6	-78.2	+135	+3.16
Substitute nitramine NO₂ for H:					
On primary amine N	+116.8	+141.3	-27.0	+45	+3.14
On secondary amine N	+115.2	+139.7	-28.6	+45	+3.11
On primary amide N	+141.7	+166.2	-2.0	+45	+3.69
On secondary amide N	+135.2	+159.7	-8.6	+45	+3.55
On carbamate N	+130.3	+154.8	-13.5	+45	+3.44
On 1st or 2nd urea N	+131.8	+156.3	-12.0	+45	+3.48
On 1st or 2nd substituted oxamide N	+140.3	+164.8	-3.5	+45	+3.66
Insert into saturated hydrocarbon chain					
Methylene CH₂	-36.3	-55.9	+146.0	+14	
Ether O	+25.2	+35.0	-32.3	+16	
Carbonyl CO	-8.4	-8.3	+58.9	+28	
Ester COO	+7.3	+17.1	+17.1	+44	
Amine NH	+12.0	+7.1	+16.8	+15	
Amide CONH	-15.9	-20.8	+80.1	+43	
Carbamate NHCOO	+2.7	+7.6	+41.4	+59	
Urea NHCONH	-17.0	-26.8	+107.8	+58	
Reaction:					
ROH + HOR' ⟶ ROR' + H₂O	+3.5	+3.5	+3.5	-18	
RCOOH + HOR' ⟶ RCOOR' + H₂O	+13.5	+13.5	+13.5	-18	
RCOOH + H₂NR' ⟶ RCONHR' + H₂O	+3.5	+3.5	+3.5	-18	
RNCO + HOR' ⟶ RNHCOOR'	-26.6	-26.6	-26.6	0	

*See Paragraph III,B,1.

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III Heat of Explosion as a Criterion of Explosive
Power (cont.)

Report No. 660

C. EXAMPLE

1. An example of the use of the method is the calculation of the change of H_E/M when a carbonyl group is substituted for a methylene group in RDX. This is shown below:
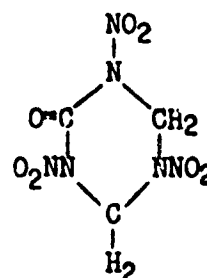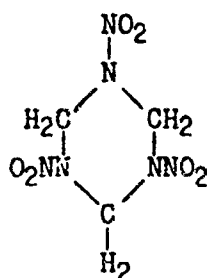
	H_E, kcal	M	
RDX	271	222	H_E/M = 1.221 kcal/g
Remove 1 methylene group	+55.9	-14	
Substitute 2 H for 2 NO_2 groups	-279.4	-90	
Remove 2 sec. amine (NH) groups	-14.2	-30	
Insert 1 urea group	-26.8	+58	
Substitute NO_2 groups on 2 urea N's	+312.6	+90	
	319.1	236	H_E/M = 1.352 kcal/g

Thus, considering H_E/M as a measure of power, there is noticeable improvement.

2. As this example illustrates, only the oxygen balance of the initial and final compounds must be considered (in this case, condition b). It can be shown that values of ΔH_E for this condition should be used for each step, even if the step gives an intermediate product in another condition (such as $C_2H_4N_2O_2$, in condition a, resulting after removal of two nitramine groups).

IV. HEATS OF EXPLOSION ON A VOLUME BASIS

A. DISCUSSION

1. Hitherto, explosive power has been rated in terms which have the dimensions of energy divided by weight. However, many practical criteria

depend on the energy available per unit volume. Table II lists the heats of explosion converted to a basis of unit volume for some of the "selected high explosives"* and for new high explosives made at Aerojet on this program. All compounds for which crystal densities (for solids) or liquid densities were available are included. Values of heats of explosion for the Aerojet compounds were calculated from the equations of Reports No. 512 and 538, using experimental rather than predicted heats of combustion.

2.   The table shows that, in general, the factors that increase heat of explosion per unit weight also increase density, so that the orders of effectiveness of these explosives are not greatly different, whether they are rated in kilocalories per gram or kilocalories per milliliter. The table also illustrates the fact that several of the new compounds are appreciably more powerful, on the basis of these properties, than the standard explosives.

3.   It is of interest to consider together the three quantities H_E, Mv, and M; H_E is molar heat of explosion, Mv is molecular volume, and M is molecular weight. Each is a sum of terms which are (within certain limitations, for H_E and Mv) constants characteristic of the structural components. For each of these quantities, a change in structure produces a change which is independent of the unaltered portion of the molecule.

4.   In making chemical changes to improve performance, an attempt is made to increase, simultaneously, the values of H_E/M, H_E/Mv, and M/Mv. These goals are inconsistent, and the inconsistency should be recognized.

5.   Confining attention to H_E/Mv, it is possible to tabulate values of ΔH_E and ΔMv for the substitution or insertion of structural groups, and to take the ratio $\Delta H_E/\Delta Mv$ as a measure of improvement. Table III is a partial list of these quantities, taken from other sections of this report. Values of ΔH_E are those calculated for condition b, in which all H has been oxidized to H_2O, and some CO has been oxidized to CO_2. These values are subject to the conditions discussed in other sections, and are additive terms only, taking no account of interactions. Table III, much more than Table II, shows strikingly how an increase in the number of plosophoric groups increases the heat of explosion per unit volume much more than it increases the heat of explosion per unit weight (cf. Table I).

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*See Table I, Report No. 512.

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IV Heats of Explosion on a Volume Basis, A (cont.)   Report No. 660

TABLE II

HEATS OF EXPLOSION ON WEIGHT AND VOLUME BASIS

(Heat of explosion in kcal/g = H_E/M;
heat of explosion in kcal/ml = $(H_E d)/M$)

Compound	Empirical Formula	H_E kcal/mole	M	Density d, g/ml	H_E/M kcal/g	$(H_E d)/(M)$ kcal/ml
(Selected high explosives from Aerojet Report No. 512, p. 9)						
Nitroglycerine	$C_3H_5N_3O_9$	342.7	227.1	1.591*	1.509	2.40
PETN	$C_5H_8N_4O_{12}$	441.7	316.2	1.77	1.397	2.47
RDX	$C_3H_6N_6O_6$	271.2	222.1	1.816	1.221	2.22
HMX	$C_4H_8N_8O_8$	349.5	296.2	1.92	1.180	2.27
DiPEHN	$C_{10}H_{16}N_6O_{19}$	566.8	524.3	1.63	1.081	1.76
EDNA	$C_2H_6N_4O_4$	145.6	150.1	1.71	0.970	1.66
Tetryl	$C_7H_5N_5O_8$	250.2	287.2	1.73	0.871	1.51
TNT	$C_7H_5N_3O_6$	143.3	227.1	1.654	0.631	1.05
(Aerojet explosive compounds from reports of this series)						
1,1,1,3,5,5,5-Heptanitro-pentane	$C_5H_5N_7O_{14}$	579.8	387.2	1.74	1.497	2.60
N-Nitro-N-3,3,3-trinitro propyl 2,2,2-trinitroethyl carbamate	$C_6H_6N_8O_{16}$	639.8	446.2	1.805	1.434	2.59
Methylene N,N'-Dinitro-N,N'-bis(trinitroethyl carbamate)	$C_7H_6N_{10}O_{20}$	673.6	550.2	1.89	1.224	2.32
bis(2,2-Dinitropropyl) nitramine	$C_6H_{10}N_6O_{10}$	333.3	326.2	1.73	1.022	1.77
3,3-Dinitro-1,5-pentane-N,N'-dinitro-N,N'-bis(trinitro-ethyl carbamate)	$C_{11}H_{12}N_{12}O_{24}$	910.2	696.3	1.76	1.307	2.30
N,3,3,5,5-Pentanitropiperidine	$C_5H_6N_6O_{10}$	414.1	310.2	1.83	1.335	2.44
N,2,2,2-Trinitroethyl-3,3,5,5-tetranitropiperidine	$C_7H_8N_8O_{14}$	580.9	428.2	1.81	1.357	2.45
3,3-Dinitro-1,5-pentane-dinitramine	$C_5H_{10}N_6O_8$	258.8	282.2	1.67	0.917	1.53
bis(3,3,3-Trinitropropyl) urea	$C_7H_{10}N_8O_{13}$	453.1	414.2	1.72	1.094	1.88
N-Nitro-bis(3,3,3-trinitro-propyl) urea	$C_7H_9N_9O_{15}$	605.6	459.2	1.75	1.319	2.31
1,1,2,2-Tetranitratomethyl-1,2-dinitroethane	$C_6H_8N_6O_{16}$	668.8	420.2	1.84	1.592	2.93

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*Liquid.

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IV Heats of Explosion on a Volume Basis, A (cont.)   Report No. 660

TABLE III

CHANGES IN HEAT OF EXPLOSION PER UNIT VOLUME
FOR SOME STRUCTURAL CHANGES

Change	ΔH_E, kcal	ΔMv, ml	$\Delta H_E/\Delta(Mv)$ kcal/ml
Substitute for H in aliphatic hydrocarbon structure:			
Nitro NO_2	+135.2	+8.5	+15.9
$(NO_2)_2$ (for 2H)	+276.4	+30.5	+9.1
$(NO_2)_3$ (for 3H)	+426.6	+51.4	+8.3
Nitramine $NHNO_2$	+141.8	+13.5	+10.5
Nitrate ester ONO_2	+190.8	+19.0	+10.0
Methyl CH_3	-55.9	+16.3	-3.4
Phenyl C_6H_5	-236.9	56.7	-4.2
Amine NH_2	+0.5	+2.1	+0.2
Insert into aliphatic chain:			
Nitramine NNO_2	+146.8	+13.5	+10.9
Amine NH	+7.1	+2.1	+3.4
Amide NHCO	-20.8	+12.8	-1.6
Carbamate NHCOO	+7.6	+21.8	+0.3

V. THE PREDICTION OF CRYSTAL DENSITY FROM STRUCTURE

A. INTRODUCTION

1. Crystal density is an important criterion of acceptability of new explosives, because of its effect on such practically important properties as loading density and detonation velocity. Quantitatively, it is desirable that new explosive compounds prepared on this program have crystal densities of 1.8 or greater.

2. An accurate prediction of the crystal density of a compound whose synthesis is being considered would thus have considerable value, and the development of such a method of prediction was undertaken. Because there

V The Prediction of Crystal Density from Structure, A (cont.) Repert No. 660

is known to be a regular dependence of molecular volume on structure in many liquid compounds, it seemed best to start by developing this relationship for the (hypothetical) liquid state. Crystal density could then be related to liquid density in a separate operation.

B. THE RELATION OF LIQUID MOLECULAR VOLUME TO CHEMICAL STRUCTURE

1. Additive Terms for Structural Components

a. For an alkyl aromatic hydrocarbon of formula C_cH_h the molecular volume at $25°C$ is expressible by the following equation:[*]

$$Mv = -4.06c + 10.20h + 12.06 + 40.2R \qquad (1)$$

in which v is specific volume, or reciprocal density, and R is the number of aromatic rings. (Actually, the equation is more general, and applies to olefinic and naphthenic hydrocarbons as well. A five- or six-membered saturated ring contributes nothing to Mv and it is only necessary to substitute $40.2/3$ times the number of double bonds, whether olefinic or aromatic, for $40.2R$ to make the equation generally applicable.)

b. It seemed likely that this equation could be extended to compounds containing functional groups by the addition of further constant terms characteristic of these groups. To test this supposition, liquid densities were compiled from Beilstein for several homologous series of the form RX or RXR'. A plot of Mv vs number of carbon atoms was then constructed for each series. In each case, the equation could be adjusted to fit the points closely by the addition of a suitable constant term. Thus additivity of molecular volumes holds well in each case.

c. The increments for certain other structural groups could not be evaluated in this way because of the lack of data, and another procedure had to be followed. The term for the gem dinitro group, for example, had to be evaluated by comparing molecular volumes of such pairs of compounds as 2,2-dinitrobutyl acrylate and n-butyl acrylate. (Basic data were taken from Beilstein, SPIA publications, Aerojet reports, etc.) In each instance there was close agreement of results from several pairs, and the value chosen as representative was accepted with confidence.

d. All increments of molecular volume obtained to date are collected in Table IV.

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[*]By correction of an expression for Mv^{20}, see R. H. Deanesly and L. T. Carleton, J. Phys. Chem. 46, 859 (1942).

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V The Prediction of Crystal Density from
Structure, B (cont.)

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TABLE IV

INCREMENTS OF MOLECULAR VOLUME FOR FUNCTIONAL GROUPS

$$Mv = -4.06c + 10.20h + 12.06 + \Sigma(\text{additive terms}) + \Sigma(\text{interaction terms})$$

Group	Additive Term
Saturated hydrocarbon	0
Alkyl mononitro	+18.7
dinitro $(NO_2)_2C$	+50.9
trinitro $(NO_2)_3C$	+82
primary or secondary amine	-8.1
nitramine	+13.5
carbamate	+15.7
secondary amide	+6.7
nitrate ester	+29.2
(Single) Aromatic ring	+40.2
mononitro	+22.2
primary amine	+5.5
secondary amine	+4.3
C-Alkyl piperidine ring	-3.3
N-Alkyl piperidine ring	+0.7

	Interaction Term
Nitrate ester on the same or adjacent C atoms	+2.0
Nitrate ester and nitro on adjacent C atoms	+3.6

V The Prediction of Crystal Density from
  Structure, B (cont.)

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2.   <u>Interaction Effects</u>

    a.   For compounds containing several functional groups, one may write

$$Mv = -4.06c + 10.20h + 12.06 + \Sigma \text{ additive terms} \qquad (2)$$

in which the summation includes separate contributions from all the functional groups. However, results of this calculation sometimes disagree with the experimentally determined molecular volumes of complex structures. For example, data are fairly plentiful* on liquid explosives containing two or more nitrate ester groups, and for compounds containing neighboring nitrate groups, densities are consistently lower than values predicted from (2).

    b.   Good agreement may be secured, however, by assigning an interaction term to the occurrence of nitrate groups on the same C atom or on adjacent C atoms. Assignment of a value of +2.0 for each such interaction results in the following good agreement between experimental and predicted densities:

Compound	Liquid Density, g/ml	
	Predicted	Experimental
Methylene glycol dinitrate	1.555	1.53
Ethylene glycol dinitrate	1.447	1.48
1,2-Propanediol dinitrate	1.367	1.376
Nitro glycerine	1.594	1.591
α-Methyl glycerine trinitrate	1.518	1.50
1,2,4-Butanetriol trinitrate	1.538	1.520

    c.   Table IV gives the term for interaction between nitrate groups, and another term for the interaction between a nitrate ester group and a nitro group on adjacent C atoms (based on the liquid density of only one compound, trimethylol nitromethane trinitrate**). The absence of interaction terms for other structures does not mean that these terms do not exist, but only that basic data for their evaluation are lacking.

    d.   Accordingly, the calculation of liquid densities from the equation

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*OSRD No. 2014: "Compilation of Data on Organic Explosives"; Picatinny Arsenal
  Technical Report No. 1740: "Properties of Explosives of Military Interest."

**OSRD No. 2014.

V The Prediction of Crystal Density from
Structure, B (cont.)

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$$hv = -4.06c + 10.20h + 12.06 + \Sigma(\text{additive terms}) + \Sigma(\text{interaction terms}) \quad (3)$$

is recommended. The values of Table IV should be used insofar as they apply, with the recognition that there may be other interaction effects, still unknown.

C.   THE RELATION OF CRYSTAL DENSITY TO LIQUID DENSITY

1.   The next step needed is a conversion of calculated liquid densities to crystal densities. The literature contains a few careful studies of the increase of volume of organic compounds on melting. Whether or not this quantity can be related to constitution remains to be determined. In any case, a simpler treatment is to plot measured crystal density vs predicted liquid density for a large number of explosive compounds, to determine whether all points can be represented by a single line.

2.   An initial search of the sources cited previously disclosed 17 compounds, differing widely in constitution, for which crystal densities had been measured and molecular volumes could be calculated from the equation. When crystal densities were plotted against predicted liquid densities for these compounds all points except three clustered about a unique straight line, with a maximum scatter of 0.08 g/ml. This comparison of measured crystal densities with values from the line is shown in Table V and Figure 1.

3.   The three discrepant compounds are m-nitro phenyl dinitromethane, erythritol tetranitrate, and dulcitol hexanitrate. In these cases, it may be considered that either the quoted experimental values are in error (e.g., by a confusion of loading density with crystal density) or the method of prediction itself is faulty. The extreme irregularity of the density of the first casts doubt on the experimental value given for this compound. On the other hand, the method of prediction may be at fault in the other two cases, particularly because of the similarity of the compounds. Possibly the treatment of interaction among nitrate groups suggested above may be inadequate for cases of large numbers of adjoining groups.

4.   In any case, on the basis of the many points showing fair agreement, provisional use of Equation (3) and of the line of Figure 1 for predicting crystal densities of new compounds is recommended. Undoubtedly the method can be refined and extended as more experimental data become available.

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V The Prediction of Crystal Density from
   Structure, C (cont.)

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TABLE V

COMPARISON OF MEASURED AND PREDICTED CRYSTAL DENSITIES

Compound	Number	Predicted Liquid d^{25}	Measured Crystal d^{25}	From Line of Figure 1 Crystal d^{25}	Δd
2,3-Dinitro-2,3-dimethylbutane	1	1.192	1.25	1.30	-0.05
2,2-Dinitropropane	2	1.199	1.26	1.31	-0.05
2,2-Dimethyl-1,3-propanediol dinitrate	3	1.276	1.38	1.37	+0.01
1,1,1-Trinitroethane	4	1.418	1.53	1.50	+0.03
m-Nitrophenyl dinitromethane	5	1.536	1.29	1.60	-0.31
bis(2,2-Dinitropropyl) nitramine	6	1.591	1.73	1.65	+0.08
2,4,6-Trinitrotoluene	7	1.603	1.654	1.66	-0.01
Ethylene dinitramine	8	1.629	1.71	1.68	+0.03
3,3-Dinitro-1,5-pentane dinitramine	9	1.635	1.67	1.68	-0.01
PETN	10	1.662	1.77	1.71	+0.06
Erythritol tetranitrate	11	1.680	1.58	1.72	-0.14
N-2,2,2-Trinitroethyl-3,3,5,5-tetranitropiperidine	12	1.712	1.81	1.75	+0.06
1,1,1,3,5,5,5-Heptanitropentane	13	1.718	1.74	1.76	-0.02
2-(3',5'-Dinitrophenyl)2-nitro-1,3-propanediol dinitrate	14	1.747	1.70	1.78	-0.08
1,1,2,2-Tetranitratomethyl-1,2-dinitroethane	15	1.766	1.84	1.80	+0.04
Dulcitol hexanitrate	16	1.777	1.62	1.81	-0.19
2,3,4,6-Tetranitroaniline	17	1.788	1.867	1.82	+0.05

V The Prediction of Crystal Density from
   Structure, C (cont.)
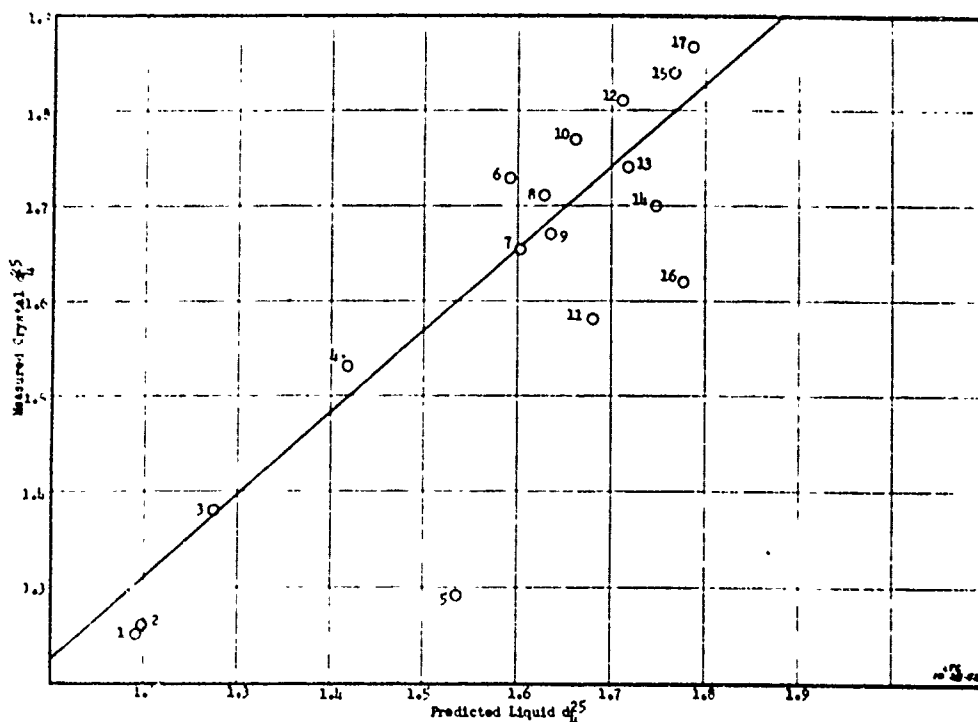
Figure 1

Relation Between Crystal Density and Liquid Density
Predicted from Equation for Explosive Compounds

D.   EXAMPLE

Use of the method may be illustrated by calculating at length the
crystal density of tetryl:

Structure: $(NO_2)_3 \phi N(NO_2) CH_3$ $C_7H_5N_5O_8$

Molecular Weight = 287.2

$$-4.06c = -28.4$$
$$+10.20h = +51.0$$
$$+12.1$$

Additive terms for ϕ ring	+10.2
for 3 NO_2 groups on ϕ ring	+66.6
for sec. amine on ϕ ring	+4.3
for substitution of NO_2 for H on N	+11.4 $\left[13.5 - 10.2 - (-8.1) \right]$

$$Mv = 157.2 \text{ ml/mole}$$

Thus, liquid d = 287.2/157.2 = 1.827 g/ml

and from the line of Figure 1, d = 1.85 g/ml (experimental, 1.73)

This disagreement is excessive, and is discussed below.

V The Prediction of Crystal Density from   Report No. 660
     Structure (cont.)

E.   INADEQUACIES OF THE METHOD

         1.   In its present state, the method is not so much faulty as incomplete.

         2.   In the example cited above, the disagreement between measured and predicted crystal densities seems to indicate that all contributions to liquid molecular volume have not yet been accounted for. Consistently low values of M_V for allied compounds suggest that interaction terms are needed for some or all of the combinations of neighboring functional groups in the trinitrophenyl amino structure.

         3.   Similar attempts to predict crystal densities of some N-nitroamides and N-nitrocarbamates and some two-ring compounds were likewise unsuccessful. Thus, great caution is needed in applying the method to structures for which it has not yet been proved.

         4.   Extension of the treatment to these cases is hampered by the scarcity of experimentally determined liquid densities of compounds containing the appropriate structures. However, it may be possible to use crystal densities to evaluate the contributions to M_V. This possibility will be investigated in the future.

VI.   CO-POLYMERIZATION OF 2,2-DINITROBUTYL ACRYLATE, 2-NITROBUTYL ACRYLATE, AND 2-NITRO-2-ETHYL-1,3-DIACRYLOXYPROPANE

     A.   EMULSION CO-POLYMERIZATION

         1.   Introduction

         In the early preparations of poly 2,2-dinitrobutyl acrylate by emulsion, before a satisfactory method of purification of the monomer had been achieved, a soft and rubbery polymer was obtained. Polymerization of the purified monomer gave a much harder polymer, which was less suitable for coating RDX. The impurities in the 2,2-dinitrobutyl acrylate which caused the polymer to be softer were thought to be 2-nitrobutyl acrylate and 2-nitro-2-ethyl-1,3-diacryloxypropane.[*] These two compounds were synthesized, so that they could be co-polymerized in varying proportions with 2,2-dinitrobutyl acrylate to determine whether this same soft polymer, which was originally obtained, could be reproduced.

         2.   Discussion

         a.   The emulsion polymerization of 2-nitrobutyl acrylate was carried out in the same manner that has been described for 2,2-dinitrobutyl

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[*] Aerojet Report No. 622, p. 58.

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VI Co-Polymerization of 2,2-Dinitrobutyl Acrylate,
    2-Nitrobutyl Acrylate, and 2-Nitro-2-ethyl-1,3-
    diacryloxypropane, A (cont.)
                               Report No. 660

acrylate.[*] Poly 2-nitrobutyl acrylate, obtained in a quantitative yield, is a soft, rubbery, acetone-insoluble polymer, in contrast with poly 2,2-dinitrobutyl acrylate, which is a hard, acetone-soluble polymer.

        b.   In the emulsion co-polymerizations of 2,2-dinitrobutyl acrylate and 2-nitrobutyl acrylate, increasing the percentage of the latter from 5 to 20% gave a softer, acetone-soluble polymer.

        c.   In the emulsion co-polymerizations of 2,2-dinitrobutyl acrylate, 2-nitrobutyl acrylate, and 2-nitro-2-ethyl-1,3-diacryloxypropane, the polymer precipitating from the emulsion was acetone-insoluble.

        d.   The previous work indicated that poly 2-nitrobutyl acrylate or a co-polymer of 2,2-dinitrobutyl acrylate (80 to 90%) and 2-nitrobutyl acrylate (10 to 20%), prepared by the emulsion technique, were softer than poly 2,2-dinitrobutyl acrylate itself. Thus, either of the latter two systems might be more suitable for the coating of RDX. It was found that the addition of 2-nitro-2-ethyl-1,3-diacryloxypropane increased the hardness of the polymer.

        3.   Experimental

        The experimental results are summarized in Table VI.

    B.   BULK CO-POLYMERIZATION

        1.   Discussion

        The bulk polymerization of 2-nitrobutyl acrylate and 2-nitrobutyl acrylate (5 to 20%) with 2,2-dinitrobutyl acrylate (80 to 95%) has resulted in a soft, gummy, acetone-soluble polymer which should be well suited for the coating of RDX from solution. The addition of 2-nitro-2-ethyl-1,3-diacryloxypropane gave a harder polymer which was acetone-insoluble.

        2.   Experimental

        The experimental results are summarized in Table VII.

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[*]Aerojet Report No. 637, p. 25.

VI Co-Polymerization of 2,2-Dinitrobutyl Acrylate,
2-Nitrobutyl Acrylate, and 2-Nitro-2-ethyl-1,3-
dimethoxypropane, B (cont.)

TABLE VI

EMULSION POLYMERIZATIONS[1] OF DNBA[2], NBA[3], DNBA AND NBA AND DIAC[4]

Emulsion No.	Monomer	Tween-40 %	(NH4)2S2O8 %	PVA %	Lecithin %	Water ml	Temp °C	Time hr	Polymer %	Remarks
N-295	DNBA	7.5	1	3	0.5	27	45	67	85	Good emulsion, polymer hard, acetone-soluble
N-296	DNBA							67	85	Good emulsion, polymer hard, acetone-soluble
N-297	NBA							41	100	Good emulsion, polymer rubbery, acetone-insoluble
N-298	NNBA							41	100	Good emulsion, polymer rubbery, acetone-insoluble
" 299	DNBA - 95% NNBA - 5%							140	94	Good emulsion, polymer hard, acetone-soluble
N-300	DNBA - 90% NBA - 10%								95	Good emulsion, polymer hard, acetone-soluble
N-301	DNBA - 85% NNBA - 15%								95	Good emulsion, polymer softer, acetone-soluble
N-302	DNBA - 80% NNBA - 20%								93	Good emulsion, polymer softer, acetone-soluble
N-306	DNBA - 89% NBA - 10% DIAC - 1%							66	--	Polymer precipitated out, acetone-insoluble
N-307	DNBA - 87% NNBA - 10% DIAC - 3%							66	--	Polymer precipitated out, acetone-insoluble
N-308	DNBA - 85% NNBA - 10% DIAC - 5%							66	--	Polymer precipitated out, acetone-insoluble
N-309	DNBA - 89% NNBA - 10% DIAC - 1%							22	76	Good emulsion, polymer soft, acetone-insoluble
N-310	DNBA - 87% NNBA - 10% DIAC - 3%							22	--	Polymer precipitated out, acetone-insoluble
N-311	DNBA - 85% NNBA - 10% DIAC - 5%							22	--	Polymer precipitated out, acetone-insoluble

(1) A total of 15 g of monomer was polymerized in 4-oz bottles by rotation in a 45°C water bath.
(2) DNBA = 2,2-Dinitrobutyl acrylate.
(3) NBA = 2-Nitrobutyl acrylate.
(4) DIAC = 2-Nitro-2-ethyl-1,3-diacryloxypropane.

VI Co-Polymerization of 2,2-Dinitrobutyl Acrylate,   Report No. 660
   2-Nitrobutyl Acrylate, and 2-Nitro-2-ethyl-1,3-
   diacryloxypropane, B (cont.)

TABLE VII

BULK POLYMERIZATIONS[1] OF MNBA, DNBA,[2] AND MNBA,[3]

DNBA AND MNBA AND DIAC[4]

DNBA %	MNBA %	DIAC %	Time hr	Temp °C	Solubility in Acetone	Remarks
—	100	—	140	45	Soluble	Polymer very soft and gummy
95	5	—	140	45	Soluble	Polymer very soft and gummy
90	10	—	140	45	Soluble	Polymer very soft and gummy
85	15	—	140	45	Soluble	Polymer very soft and gummy
80	20	—	140	45	Soluble	Polymer very soft and gummy
89	10	1	72	45	Insoluble	Polymer firm but soft
87	10	3	72	45	Insoluble	Polymer very soft and easily crumbled
85	10	5	72	45	Insoluble	Polymer firm and solid

[1] All samples catalyzed with 1% MAKP, cured in test tubes flushed with N_2.

[2] DNBA = 2,2-Dinitrobutyl acrylate.

[3] MNBA = 2-Nitrobutyl acrylate.

[4] DIAC = 2-Nitro-2-ethyl-1,3-diacryloxypropane.

VII. DESENSITIZATION OF RDX

A. BY COATING FROM EMULSION

1. Discussion

a. The emulsion coating of RDX with poly 2,2-dinitrobutyl acrylate has not significantly raised the impact stability of the RDX. Inasmuch as poly 2,2-dinitrobutyl acrylate is a hard polymer and poly 2-nitrobutyl acrylate is a soft and rubbery polymer, it was thought that the latter polymer or a co-polymer of the two would be better suited for coating.

b. The impact stability of RDX coated from emulsion with poly 2-nitrobutyl acrylate or a co-polymer of 2-nitrobutyl acrylate (5 to 20%) and 2,2-dinitrobutyl acrylate (80 to 95%) ranged from 30 to 65 cm/2 kg, thus showing no improvement over the previous work. However, it is believed that the inherent difficulty in applying a uniform coating is due to the emulsion technique rather than to the coating agent employed. This is borne out by the more successful results obtained when these same coating agents were applied from solution (see VII,B).

2. Experimental

The experimental results are summarized in Table VIII.

TABLE VIII

DESENSITIZATION OF RDX

Sample No.	Method	Polymer or Coating Agent	Polymer Source	Polymer %	Span-85 %	Temp °C	Water to RDX Ratio	I.S. (cm/2 kg) REC	5/0 Sandpaper	Remarks
S-206	A	Beeswax	—	10	1	90	2/1	>100	95 to 100	Small, soft pellets
S-207		(1)	—	10			2/1	60 to 65	—	Small, hard pellets
S-208		(2)	—	10			3/1	50 to 55	—	Small, hard pellets
S-209		(3)	—	8			2/1	40 to 45	—	Small, hard pellets
S-210		(4)	—	4			2/1	45 to 50	—	Looks like RDX
S-211		(5)	—	10			2/1	65 to 70	—	Looks like RDX but softer
S-213		Beeswax-25% DNBA-75%	—	10			2/1	45 to 50	—	Small pellets
S-222		90% DNBA(6) 10% MNBA(7)	Bulk polymer	10		85	2.5/1	>100	30 to 35	Small pellets
S-224		90% DNBA 10% MNBA		7.5	2.5			>100	45	Large pellets
S-223		80% DNBA 20% MNBA		10	1.0			90 to 95	25 to 30	Large pellets
S-225		MNBA		8	1.0			100	—	Small, even pellets
S-227		MNBA		5	2.5			>100	35 to 40	Solvent-to-polymer ratio 47/1
S-228		95% DNBA 5% MNBA		10	1			>100	30	Solvent-to-polymer ratio 15/1; small pellets
S-229		90% DNBA 10% MNBA		10	1			>100	30	Solvent-to-polymer ratio 15/1; small pellets
S-230		95% DNBA 5% MNBA		5	2			>100	40	Solvent-to-polymer ratio 30/1; small pellets
S-231		90% DNBA 10% MNBA		5	2			>100	35	Solvent-to-polymer ratio 30/1; small pellets
S-233				10	2.5			>100	30	Polymer ratio 12/1; small pellets
S-234					2.5			>100	50	Polymer ratio 12/1; large pellets
S-235					2.5			>100	45	Polymer ratio 6/1; small pellets
S-236					2.5			>100	20	Polymer ratio 10/1; small pellets
S-237					2.5			>100	30	Polymer ratio 25/1; small pellets
S-212	B	DNBA	N-295		1	90	2/1	50 to 55	—	Very caked
S-214		MNBA	N-297		1	80	2/1	30 to 35	—	Very caked
S-215		DNBA	N-298		1	80	2/1	60 to 65	—	Somewhat caked
S-216		MNBA	N-297		1	20	2/1	50 to 55	—	Looks like RDX
S-217		MNBA	N-298		1	20	2/1	60 to 65	—	Looks like RDX
S-218		95% DNBA 5% MNBA	N-299		1.0	Ambient	2.5/1	35 to 40	—	Looks like RDX
S-219		90% DNBA 10% MNBA	N-300					15 to 20	—	Looks like RDX
S-220		85% DNBA 15% MNBA	N-301					15 to 20	—	Looks like RDX
S-221		80% DNBA 20% MNBA	N-302					30 to 35	—	Looks like RDX
S-232		89% DNBA 10% MNBA 1% DIAC(8)	N-309					100	20	Small, fluffy particles

(1) Dimethyl 4,4,6,8,8-pentanitroundecanedioate
(2) Dimethyl 4,4,6,6,8,8-hexanitroundecanedioate
(3) 4,4,8,8,8-Pentanitroundecane
(4) Dimethyl 4,4,6,8,8-pentanitro-6-aza-undecanedioate
(5) 2,2-Dinitropropane
(6) DNBA = 2,7-Dinitrobutyl acrylate
(7) MNBA = 2-Nitrobutyl acrylate
(8) DIAC = 2-Nitro-2-ethyl-1,3-diacryloxypropane

Method A

To a 500-ml resin pot fitted with mechanical stirrer, thermometer, and dropping funnel was added 50 ml water. Stirring was started, and the water was heated to 85°C with the steam bath. Span 85 was added, and stirred 2 min; 20 g RDX was added, and stirred 5 min. The polymer was dissolved in 15 ml methyl isobutyl ketone and added dropwise through a dropping funnel. Stirring was continued until the addition was complete and all of the solvent had been distilled azeotropically. Small amounts of water were added intermittently to keep the water level up. The RDX was filtered off, water-washed, and dried.

Method B

In a 500-ml resin pot fitted with mechanical stirrer, thermometer, and dropping funnel was placed 50 ml water. Stirring was started and the Span 85 was added and stirred approximately 2 min. 20 g of RDX was then added, and stirred 5 min. The emulsion was then added from a pipette (dropwise) to the rapidly stirring slurry. The mixture was allowed to stir 5 min after addition was complete. The RDX was then filtered off, washed with water, and dried.

B.   BY COATING FROM SOLUTION

1.   Discussion

a.   RDX was coated at 80 to 90°C with a solution of a co-polymer of 2-nitrobutyl acrylate (5 to 20%) and 2,2-dinitrobutyl acrylate (80 to 95%), using the same technique employed for the preparation of Composition A. The impact stabilities of the coated RDX samples were greater than 100 cm/2 kg, and ranged from 25 to 50 cm/2 kg on 5/0 sandpaper (Composition A = 55 cm/2 kg). The best results were obtained using a 10% coating of a co-polymer containing 90% 2,2-dinitrobutyl acrylate and 10% 2-nitrobutyl acrylate with 2.5% Span 85 as a wetting agent. The percentage of Span 85 used was critical; with amounts less than 2.5%, poorer desensitization was obtained. Microphotographs of this coated RDX and RDX itself are shown in Figures 2 and 3, respectively. The rate of addition in the co-polymer solution or its concentration in the aqueous RDX slurry at any given time appears to be critical in determining the particle size and impact stability of the coated RDX. That is, if the concentration of the co-polymer in the slurry is high, the coated RDX particles agglomerate with the formation of large pellets. Two 25-g samples of coated RDX (S-234 and S-235) were submitted to the Naval Ordnance Laboratory for evaluation.

b.   The effectiveness of the solution coating of RDX with dimethyl 4,4,6,8,8-pentanitro-undecanedioate, dimethyl 4,4,6,6,8,8-hexanitro-undecanedioate, 4,4,5,8,8-pentanitro-undecane, dimethyl 4,4,6,8,8-pentanitro-6-aza-undecanedioate, and 2,2-dinitropropane was determined.* In no case was there any significant increase in the impact stability of the RDX.

2.   Experimental

The experimental results are summarized in Table VIII.

C.   COATING WITH MONOMERS AND POLYMERIZING

1.   Discussion

a.   Work of the previous quarter** had shown a promising degree of desensitization of RDX, achieved by coating with dinitrobutyl acrylate monomer and curing the coating.

b.   Further investigation showed that these products had poor impact stabilities when tested on sandpaper. However, the method warranted additional study, and a systematic program of experiments was undertaken. The series was devised to vary, on the one hand, the identity of the monomer or monomers, and on the other hand, the mode of application.

c.   Samples were prepared in which dinitrobutyl acrylate, mononitrobutyl acrylate, and a mixture of dinitrobutyl acrylate and acrylic acid

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*Aerojet Reports No. 621 and 638.

**Aerojet Report No. 637.

Figure 2

RDX + 10% Co-polymer of DNBA(90%) and MNBA(10%) .
I.S. = 45 cm/2 kg on 5/0 Sandpaper (35X)

Figure 3

RDX
I.S. = 30 cm/2 kg (50X)

(for co-polymerization) were applied, each under several different conditions. Mononitrobutyl acrylate was selected for trial because it has recently become available in pure form. Acrylic acid is of interest because there is much evidence of the affinity of hydroxyl groups – and presumably of carboxyl groups – for RDX; a co-polymer containing the latter group might give a more tenacious coating than the dinitrobutyl acrylate homo-polymer. If this co-polymer were to give good desensitization, other co-polymers of hydroxy acrylates should be investigated.

        d.   The monomers were applied either undiluted or dissolved in cyclohexane or in ethanol. The selection of these solvents was based on a combination of several factors. Each dissolves the monomers, and each precipitates out polymer above a certain molecular weight. This limiting molecular weight appears to be much lower for cyclohexane than for ethanol. Finally, the ethanol itself has a high heat of wetting RDX and a low free energy of wetting;* presumably both values are low for cyclohexane.

        e.   It should be noted that the tendency of a solute to wet the surface preferentially, displacing the solvent, is not determined simply by a comparison of free energies of wetting of pure solute and pure solvent. In such a system, the thermodynamics of demixing each component from the solution must also be taken into account.

        f.   Paralleling each preparation, whether with monomer alone or with monomer solution, another was set up in the same way except for the addition of 1% Alox 600 wax (RDX basis) as a surface active agent. This agent was selected because of its success in other RDX coating applications and because, following the experience with Span 85, commercially available esters of long-chain acids are suspected of retarding polymerization.

        g.   At the outset, it was not known what concentrations of monomer in the solutions would precipitate an adequate amount of polymer for coating. To give some measure of the amounts necessary, blank preparations of monomer solutions, containing no RDX, were set up alongside the coating preparations. It would have been preferable to investigate this effect first, but to save time it was necessary to perform the experiments simultaneously. A series of experiments were first performed at one concentration, 0.15 g/2 ml solvent; after this was completed, the amounts of polymer produced were seen to be probably inadequate in many of the samples. Thereupon another series, in which the concentration was quadrupled by doubling the solute weights and halving the solvent volumes, was set up. However, the extents of polymerization in all these blank solutions were too erratic to be v. y informative.

        h.   Impact stability tests were performed on all products of the various treatments of RDX. The results showed:

        (1)   No observable variation with the monomer

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*Evans Research and Development Corporation Progress Report II, "Studies on Surface Properties of High Explosives."

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(2)   Possible variation with the mode of application. However, in any case, such poor improvement of stability resulted that the effect of this factor is not worth further investigation.

i.   These results also show that for some samples more than one value of the height for 50% shots is obtained on the impact tester. This effect will be discussed at length in a later section. However, it must be mentioned here because it casts doubt on some of the high values of impact stability reported earlier for specimens made by curing monomers directly on RDX.

j.   Thus, the principal conclusion from this series of measurements is that results of using this technique were uniformly poor.

2.   Experimental

a.   Impact stabilities of samples of RDX desensitized by coating with dinitrobutyl acrylate monomer and curing * were redetermined on 5/0 sandpaper in the Bureau of Mines machine. The results are:

Coating	Surface Preparation	Impact Stability, cm/2 kg	
		Previously Reported	On Sandpaper
10% DNBA	—	80 to 85	30
11% DNBA	3.1% Silicone fluid over 1.0% Span 85	95 to 100	30 to 35

b.   In other preparations, mixtures of dinitrobutyl acrylate with methyl acrylate and n-butyl acrylate respectively, were applied to the surface of 1-g portions of RDX (with no surface active agent). The ingredients were introduced into small vials and mixed by thorough rolling. The monomer-coated RDX was transferred to test tubes, and the coating was cured for two to three days at 45°C, then for two to three days at 65°C. The products were vacuum treated for at least three days to remove unreacted monomer, and then tested for impact stability, with the following results:

Coating	Impact Stability, cm/2 kg
10% of 50/50% DNBA/MA	50
10% of 50/50% DNBA/n-BA	50

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* As previously described in Aerojet Report No. 637.

      c.   For further study of this technique, a systematic set of preparations was made. The following monomers were selected as coating materials:

      (1)   2,2-Dinitrobutyl acrylate

      (2)   2-Nitrobutyl acrylate

      (3)   78.0% 2,2-Dinitrobutyl acrylate + 22.0% acrylic acid

      d.   Using 1-g quantities of RDX in each preparation, each of these starting materials was applied in each of the following ways:

      (1)   To RDX, dried in the usual manner by rolling in a vial for several hours: 0.10 g monomer

      (2)   As in (1), with 1% (RDX basis) Alox 600 wax added

      (3)   To RDX freshly vacuum-dried after washing twice with methanol and three times with hexane: 0.10 g monomer

      (4)   In ethanol solution, 0.15 g/2 ml, in a glass tube filled with nitrogen and sealed off

      (5)   As in (4), with 1% Alox 600 wax added

      (6)   In cyclohexane solution, 0.15 g/2 ml

      (7)   As in (6), with 1% Alox 600 wax added

      (8)   In ethanol solution: 0.30 g/1 ml

      (9)   As in (8), with 1% Alox 600 added

      (10)   In cyclohexane solution: 0.30 g/1 ml

      (11)   As in (10), with 1% Alox 600 added

      e.   All preparations were cured three days at 45°C, and those containing solvent were mixed by continuous agitation during this period, then cured for three additional days at 65°C. All samples were then dried under vacuum for at least six days, after opening the tubes of samples containing solvent and decanting off the solution phases.

      f.   Using the Bureau of Mines impact tester, impact stabilities were determined on the products. Results are given in Table IX. In cases of more than one height for 50% shots both high and low values are given.

TABLE IX

IMPACT STABILITIES OF RDX DESENSITIZED BY COATING WITH MONOMERS AND CURING

Monomers are: (1) Dinitrobutyl acrylate   (3) 78% Dinitrobutyl acrylate
               (2) 2-Nitrobutyl acrylate   22% Acrylic acid

Mode of Application per 1.0 g RDX	Impact Stabilities, cm/2 kg		
	(1)	(2)	(3)
1 0.10 g monomer on RDX	>100[a] 30[b]	45 to 50	55 to 60
2 0.10 g monomer on RDX + 1% Alox 600 wax	60	60 to 65	65
3 0.10 g on specially dried RDX	50	55 to 75	60 to 65
4 0.15 g monomer/2 ml ethanol	45	35 to 40	40 to 45
5 0.15 g monomer/2 ml ethanol + 1% Alox 600 wax	40 to 45	30 to 35	40 to 45
6 0.15 g monomer/2 ml cyclohexane	40 to 50	55 to 60	40
7 0.15 g monomer/2 ml cyclohexane + 1% Alox 600 wax	60	30	35 to 40
8 0.30 g monomer/1 ml ethanol	lost	55 to 60	>100[a] 45 to 50[b]
9 0.30 g monomer/1 ml ethanol + 1% Alox 600 wax	>95[a] 30[b]	45 to 50	>100[a] 40 to 45[b]
10 0.30 g monomer/1 ml cyclohexane	45 to 50	35 to 40	40 to 45
11 0.30 g monomer/1 ml cyclohexane + 1% Alox 600 wax	>100[a] 60[b]	<20	20

(a) and (b) are two heights obtained for 50% shots on impact.

      g.   The products were usually sticky masses of separable crystals. However, in some of the preparations using 0.30 g monomer/1 ml solvent/g of RDX, polymerization took place to such an extent that the products were intractable lumps.

      h.   In addition, blank preparations were set up, in which each monomeric starting material was dissolved in each solvent, at each of the two concentrations. These were cured along with the RDX coating preparations. After the curing period, they were observed for signs of polymeric precipitates, with the following results:

Monomer	(1)	(2)	(3)
0.15 g/2 ml ethanol:	—	Marked	Slight
0.15 g/2 ml cyclohexane:	—	Slight	Slight
0.30 g/1 ml ethanol:	Marked	Slight	Little or none
0.30 g/1 ml cyclohexane:	Marked	Marked	Marked

D.   EVALUATION OF SURFACE ACTIVE AGENTS, AND PROPOSED FUTURE WORK

1.   Discussion

a.   On the whole, the best consistent results in desensitizing RDX appear to have been obtained by coating from solution, either cold, or by the method of preparing Composition A. Results from these methods show large variation with the materials used, suggesting that further improvement is possible by the use of still better materials.

b.   Either the nitro-compound coating or the surface active agent, or both, can be changed. There has been comparatively little time for the development of new coating materials. On the other hand, many surface active agents are commercially available and ready for immediate trial. The Atlas Powder Co. has recently provided about three dozen agents for evaluation. It is reasonable to experiment first with varying the agent rather than varying the coating material, and under present plans, these evaluations will be performed next.

c.   The choice of an evaluation test is a problem. Measurements of heats and free energies of wetting give fundamental results, but define only part of the practical operation, in not taking account of the thermodynamic effects of demixing from the liquid system. Moreover, the coating operation is complicated by the fact that two substances are deposited simultaneously on the crystal surface. On the other hand, a direct test could be made by preparing specimens of desensitized RDX in a standardized procedure, varying only the agent used, and measuring impact stabilities. This procedure has the disadvantage that it rates surface active agent-coating combinations, and these ratings may not be parallel for different coatings. It is also subject to any criticisms applying to the particular impact test employed.

d.   The almost complete adsorption of Span 85 in an experiment on coating RDX by the solution process was described earlier.* (The adsorbed Span was recovered by extraction.) This suggests the use of extent of adsorption as a means of rating surface active agents. The method seems free from objection, but whether it gives results that correlate with desensitization remains to be determined.

e.   A few trials were made of the adsorption of agent on RDX from a standard aqueous medium. The amount of Span 85 adsorbed was appreciable and reasonably reproducible. Span 85 has been, in general, the best surface active agent used to date. In contrast, adsorption of two other agents was almost negligible. A large number of agents will be characterized in this way, but first an attempt will be made to change the experimental conditions in order to enlarge the spread of adsorption by raising the percentage adsorbed that is possible with "good" agents.

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*Aerojet Report No. 589.

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2. Experimental

a. In a preliminary experiment, it was established that Span 85 applied to dry RDX can be recovered quantitatively by Soxhlet extraction with carbon tetrachloride, followed by stripping the extract of solvent.

b. Approximately 0.15 g of agent was weighed into a 100-ml round-bottomed flask, and dissolved in exactly 5 ml ethanol. The solution was agitated with a glass stirrer and 10 ml water was pipetted in. Depending on the agent, a clouded suspension or a clear solution resulted. Then 3.00 g dry RDX was added, and the slurry was stirred for 5 min. It was transferred to a vacuum filter funnel without washing, and the solid was filtered for 10 min, to remove most of the adherent liquid. It was subsequently vacuum-dried in a desiccator for at least an hour.

c. The dried solid was weighed into an extraction thimble, and Soxhlet-extracted for 1.5 hr with carbon tetrachloride. The extract was filtered (to remove RDX) into a tared flask of special conical shape, which was then attached to a short distillation column. Solvent was distilled off under a partial vacuum, with special pains taken to expel the last traces by finally removing the flask, heating in an oven at 80°C for 1 hr, and then cooling in a desiccator under vacuum. The flask was weighed again to give the weight of residue. The percentage recovery was calculated by correcting for the loss of solids in transferring.

d. The table below gives the amount of surface active agent adsorbed on RDX, expressed as percent recovered, for Span 85 (three trials, to test reproducibility) and two other Atlas surface active agents.

Agent	Appearance in Ethanol-Water	Recovery, %
Span 85: sorbitan trioleate	Milky suspension	29, 21, 24
G-3910: a polyoxyethylene fatty alcohol	Faintly cloudy, foamy solution	3
Tween 20: polyoxyethylene sorbitan monolaurate	Clear, foamy solution	6

E. THE OCCURRENCE OF MULTIPL IMPACT-STABILITY VALUES

1. Discussion

a. Other workers[*] in the field of impact stability determination have reported instances in which a substance gave one low height

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[*]NavORD Report 85-46: "Final Report on Comparison Test of Impact Sensitivity of Military Explosives," p. 35.

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for 50% shots, then a region of small-percentage shots above this height, and a second height for 50% shots much greater than the first. Similar behavior seems to be evidenced in the work described in Paragraph VI,C, and double values of impact stability are reported on several samples.

b.   A careful study of this effect was made on separate samples prepared by spreading monomeric dinitrobutyl acrylate on the surface of P^X and curing. In the impact test, weighed charges were used and ten trials, in contrast to the usual six, were made at each height. The results showed that there was no continuous increase of the tendency to shoot with increasing height. Instead, a plot of percentage shots against height indicated one apparent maximum (though short of 50% shots) in the neighborhood of 50 cm, followed by a dip in the curve, and then another rise at about 80 cm, followed by another dip.

c.   This tendency to show a maximum at a low as well as a high scale reading is undoubtedly present in many samples prepared by this technique. In some cases the first maximum is pronounced; in others it does not rise above 50% shots, and may escape detection. In any case, it is obviously unsatisfactory to characterize one of these materials by a single value of the height of 50% shots.

2.   Experimental

Ten percent of catalyzed dinitrobutyl acrylate monomer was added to 3 g RDX, and the mixture was rolled in a vial for several hours to assure uniform coating. It was then cured for four days at $45^\circ C$ and two days at $65^\circ C$, and finally vacuum-treated for five days to remove light fractions. Weighed samples (20 ± 3 mg) of the product were tested for impact stability on the Bureau of Mines machines at intervals of 10 cm, making 10 trials at each height. The results are given below:

Height, cm	30	40	50	60	70	80	90	100
% Shots:	10	20	35	15	35	35	30	10

VIII. SAFETY PRACTICE

A.   DISCUSSION

1.   For the most part, the safety shields that have been employed in this laboratory* are the standard Fisher safety-glass shields. The shields are composed of two 30 x 14 in. layers of laminated safety glass totaling 0.25 in. in thickness, and are mounted in an aluminum frame which is secured by

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*Aerojet Report No. 468 (15 September 1950), p. 60.

two metal bases. Past experience has indicated that this type of shield does not offer adequate protection to the personnel working on highly explosive compounds. This difficulty can be overcome by the use of 0.5- to 1.0-in.-thick bullet-resistant laminated plate glass, composed of three to five layers.* However, these thick shields are very heavy and rather difficult to move, and thus are best used where they can be permanently mounted.

2.   A new type of safety shield has now been designed which will offer the same protection as the very thick shields mentioned above and also possess the advantage of being much lighter in weight and thus much more easily adaptable for general laboratory use. This shield, Figure 4, consists of the standard metal form containing two parallel channels one inch apart. Two sheets of the standard 0.25-in. laminated safety glass are inserted in the parallel channels. The efficiency of this type of shield is due to the one inch of air space provided between the two sheets. The force of the explosion is thus greatly dissipated by the time the shock waves hit the second shield. This was substantiated by the following experiments, which were carried out at a distance of 4 in. from the shield.

a.   The effect of a No. 6 and No. 10 blasting cap on the front shield is shown in the upper left and upper right of Figure 5. The rear shields were unaffected.

b.   The explosion of 5 ml of Jetex (nitromethane sensitized with amine) with a No. 8 blasting cap caused complete penetration of a single shield, whereas with the double shield, the front shield was shattered but not penetrated, and the rear shield was hardly affected. This is shown in Figures 5 and 6.

c.   The effect of the explosion of 10 ml Jetex on the double shield is shown in Figure 7. The front shield was shattered but not penetrated.

3.   The use of this new type of safety shield is recommended for the following reasons:

a.   It offers adequate protection for work with highly explosive compounds, in the form of a lightweight shield which is convenient and easy to handle.

b.   The metal forms can conveniently be made to any desired size and the safety glass ordered to fit. Replacement of shattered shields is merely a matter of sliding one shield out of the channel and putting another in.

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*Taylor and Johnson, Chem. Eng. News 30, No. 44, 3 November 1952, p. 4668.

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Figure 4

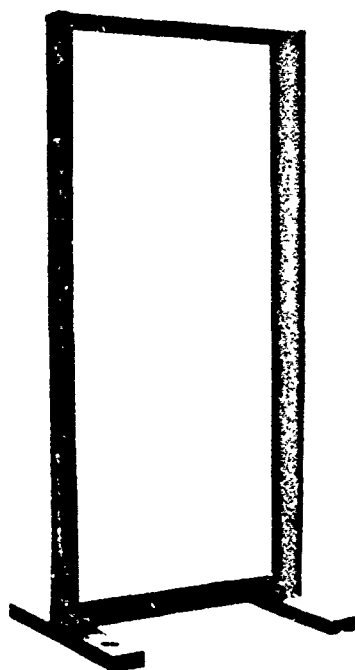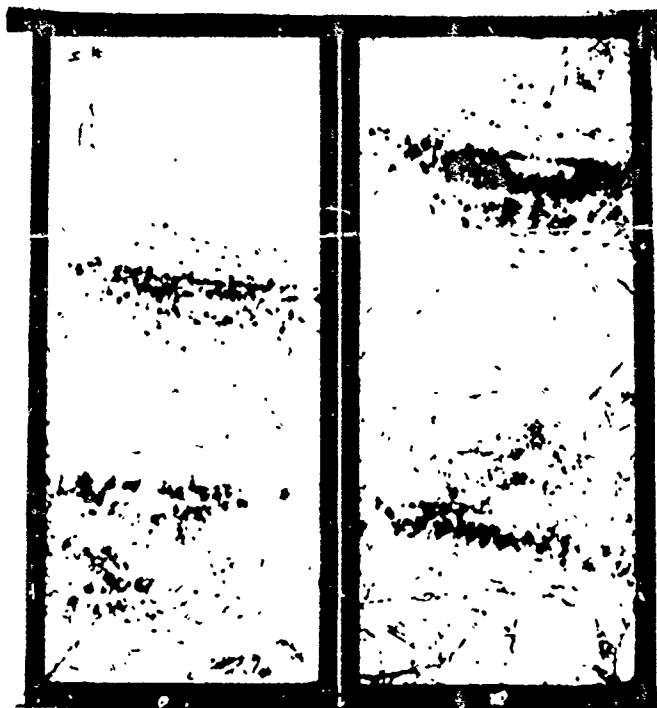New Safety Frame with Double Channels

Figure 5

Upper Left - Front shield after explosion of No. 6 blasting cap; rear shield
            unaffected
Upper Right - Front shield after explosion of No. 10 blasting cap; rear shield
            unaffected
Lower Left - Single shield after explosion of 5 ml Jetex
Lower Right - Front shield after explosion of 5 ml Jetex, very little effect
            on rear shield

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Figure 6
Close-up View of Single Shield After Explosion of 5 ml of Jetex

Figure 7
Left - Front shield after explosion of 10 ml Jetex
Right - Rear shield after explosion of 10 ml Jetex

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